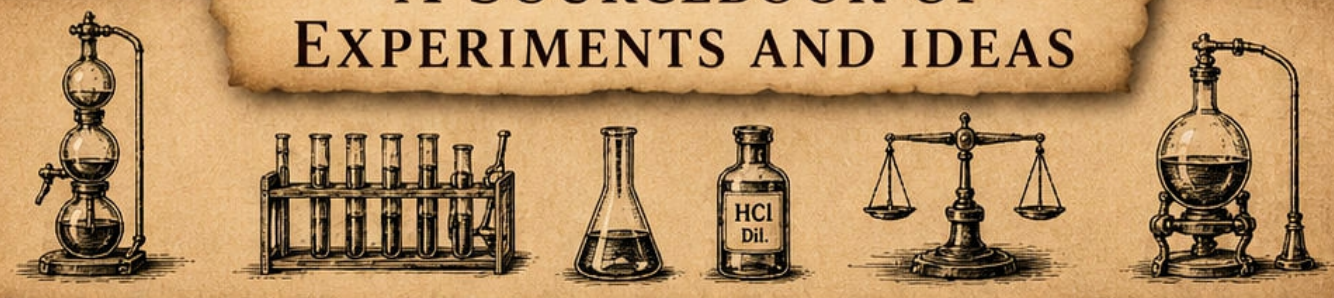
THE PRACTICAL CHEMISTRY LABORATORY

A Sourcebook of Experiments and Ideas



Marc Hallet

Inside front cover

This page intentionally left blank

BOMBS AND EXPLOSIVES

The author has taken care not to provide any information that might enable the manufacture of bombs or explosives that could easily be used for terrorist purposes or other criminal activities.

Nothing in this book is intended to encourage or facilitate such practices. On the contrary, some of the experiments described are presented solely for educational and scientific purposes. Their characteristics, methods of preparation, and inherent instability make them wholly unsuitable for the construction of destructive devices.

Anyone wishing to become an amateur killer will find no advantage in reading further.

THE PRACTICAL CHEMISTRY LABORATORY

A SOURCEBOOK OF EXPERIMENTS AND IDEAS

MARC HALLET

This book is distributed free of charge
and may be reproduced freely
for the intellectual benefit of as many people as possible.
The author nevertheless retains his moral rights.

As the author writes primarily in French, he called on ChatGPT to assist him in preparing the English version of this book. The reader is therefore kindly asked to forgive any errors in grammar, spelling, or even punctuation that may remain in the translation and layout of a work of this length.

I dedicate this book to Rose,
my beloved wife
and appreciative companion
in my laboratory work.

This page intentionally left blank

Table of Contents

Preface 1
Introduction 3
Confusions, Imprecisions, and Errors 5

Chapter 1 - Laboratory Equipment
1.1 Laboratory Layout and Workspace Design 15
1.2 Useful Equipment 17
1.2.1 Laboratory Stands 17
1.2.2 Common Laboratory Glassware 18
1.2.3 Tubing 24
1.2.4 Stoppers 25
1.2.5 PTFE (Teflon) 27
1.2.6 Heating Equipment 29
1.2.7 The Epiradiator 32
1.2.8 Stirrers 33
1.2.9 Distillation and Cooling 37
1.2.10 Filtration 42
1.2.11 Drying 44
1.2.12 High-Temperature Heating of Solids 45
1.2.13 Chemicals 46
1.2.14 Storage Bottles 47
1.2.15 Some Special Storage Methods 49
1.2.16 Practical Tips from the Past 53

Chapter 2 - A Little Pedagogy 55
2.1 Demonstration Experiments 55
2.2 Pseudo-Alchemy 64
2.3 Diffusion and Cyclic Reactions 65
2.4 Osmosis and Surface Tension 68
2.5 Mineral Gardens 69

Chapter 3 - Colour Indicators and Reagents
3.1 Colour Indicators 71
Red Cabbage Juice - Privet Berry Juice - Elderberry Juice - Brazilwood (Pernambuco Wood) - Violet Syrup - Cochineal Carmine - Phenolphthalein - Methyl Orange - Bromothymol Blue
3.2 Specific Reagents 73
For Ammonia and Ammonium Salts (Nessler's Reagent) - For Chlorine and Bromine - For Ferric Salts - For Calcium Salts - For Magnesium Salts - For Phosphates - For Carbonates - For Nitrates and Nitrites - For Alkali Formates and Formic Acid - For Aldehydes - For Glucose (Fehling's Solution) - For Iodine - Differentiating Sulfates and Sulfites
3.3 Polyvalent Reagents 77
Formaldehyde + H_2SO_4 - Sodium Hypobromite - Dry Turmeric Paper - Logwood Infusion - Potassium Ferrocyanide - (Pyro)Gallic Acid) - Ammonium Thiocarbonate - Sodium Thiosulfate (Hyposulfite) - Ammonium Mercuric Thiocyanate Reagent - Resorcinol Reagent

Chapter 4 - Preparation and Use of Gases
4.1 Continuous Gas Generators 81
4.2 Methods for Preparing Gases 86
Oxygen - Ozone - Hydrogen - Hydrogen Chloride or Hydrochloric Acid - Chlorine - Chlorine Dioxide - Bromine - Hydrogen Iodide or Hydroiodic Acid - Hydrogen Bromide or Hydrobromic Acid - Ammonia - Hydrogen Sulfide or Hydrosulfuric Acid - Hydrogen Selenide - Carbon Monoxide - Carbon Dioxide or Carbonic Acid - Sulfur Dioxide or Sulfurous Acid - Nitrogen - Nitric Oxide - Nitrogen Dioxide, Dinitrogen Tetroxide, Dinitrogen Trioxide - Nitrous Oxide - Phosphine - Boron Trifluoride - Methane - Acetylene - Ethylene - Ethyl Chloride - Methyl Nitrite
4.3 The Equipment to Use 111
4.3.1 Collecting Gas by Displacement of Air 112
4.3.2 Collecting Gas by Displacement of a Liquid 112

Chapter 5 - Useful Preparations 115
Phenolphthalein - Soda Lime and Potash Lime - Alcoholic Potash - Sulfuric Acid-Alcohol Mixtures - Tincture of Iodine - Logwood Tincture - 48% Hydrobromic Acid Solution - Nitrous or Fuming Nitric Acid - Aqua Regia - Oxalic Acid - Selenious Acid - Chromic Anhydride - Chromosulfuric Acid Mixture - Sodium Hypobromite Solution - Sodium Aluminate - Increasing the Concentration of Hydrogen Peroxide - Tin(II) Chloride and Tin(IV) Chloride - Copper(I) Chloride - Ferrous Sulfate and Ferrous Chloride Solutions - Mercurous(I) Nitrate - Mercuric(II) Nitrate - Copper Carbonate - Sodium or Ammonium Sulfide (and Polysulfide) Solutions - Potassium or Sodium Thiocarbonate (Sulfocarbonate) - Calcium Thiocarbonate (Sulfocarbonate) - Magnesium Thiocarbonate (Sulfocarbonate) - Ammonium Thiocarbonate (Sulfocarbonate) - Sodium or Potassium Thiocyanate (Sulfocyanate)

Chapter 6 - High Solubility of Certain Gases 133

Chapter 7 - Combustion of Gases 137
Ammonia - Hydrogen - Carbon Monoxide - Acetylene - Ethyl Chloride

Chapter 8 - Reactions Between Gases
8.1 With at Least Hydrogen 141
8.2 With at Least One Halogen 141
8.3 With at Least SO_2 147
8.4 With at Least Ammonia 149
8.5 With NO or NO_2 152

Chapter 9 - Reactions Between a Gas and a Liquid or a Liquid containing Solid Particles
9.1 Air or Oxygen 153
9.2 Hydrogen or Nascent Hydrogen 157
9.3 HBr, HI, I_2, Br_2, and Cl_2 158
9.3.1 Bleaching Chlorides and Hypochlorous Acid 173
9.4 Hydrochloric Acid 178
9.5 SO_2 180
9.6 CO 186
9.7 CO_2 187
9.8 H_2S 189

9.9 NH_3 193
9.10 NO, NO_2, N_2O_3 195
9.11 C_2H_2 197
9.12 C_2H_4 198

Chapter 10 - Reactions Between a Gas and a Solid
10.1 Reactions with Air, Oxygen and Hydrogen 199
10.2 Reactions with Halogens 204
10.2.1 Chlorine Dioxide 221
10.3 HCl 222
10.4 SO_2 224
10.5 NH_3 227
10.6 CO and CO_2 230
10.7 H_2S 232
10.8 NO, NO_2, N_2O_3 233
10.9 N_2O 234
10.10 C_2H_2 236
10.11 In Steam 236
10.12 Acetone or Alcohol Vapors 236

Chapter 11 - Liquefaction of a Gas 239

Chapter 12 - Cold Reactions (Liquids + Solids or Liquids + Liquids)
12.1 Reactions Involving Metals or Metalloids 241
Sodium, Potassium and Calcium - Iron - Zinc - Copper - Nickel - Tin - Lead - Magnesium - Aluminium - Chromium - Cobalt - Cadmium - Manganese - Boron - Bismuth - Vanadium - Molybdenum - Titanium - Tungsten - Mercury - Silver - Gold - Antimony - Arsenic - Phosphorus - Selenium
12.2 Reactions Involving Halogens and Halides 266
Chlorine - Bromine - Iodine - Hydrobromic and Hydroiodic Acids - Bromides, Iodides and Iodates
12.3 Reactions Involving Mineral Salts 275
Calcium, Sodium, Potassium, and Ammonium Salts - Iron Salts (II) and (III) - Copper Salts (I) and (II) - Zinc Salts - Lead Salts - Tin Salts - Nickel Salts - Aluminium and Magnesium Salts - Cobalt Salts - Barium, Cadmium, and Bismuth Salts - Lithium, Strontium, and Cerium Salts - Mercury Salts - Silver Salts - Gold Salts - Manganese Salts, Manganates, and Potassium Permanganate - Chromium Salts, Chromates, and Dichromates - Vanadium Salts and Vanadates - Titanium Salts - Molybdenum Salts - Tungsten Salts - Borates and Perborates - Antimony Salts - Arsenates and Arsenites - Other Types of Mineral Salts
12.4 Reactions with Fuming Nitric Acid 340
12.5 Simple Reactions with Organic Substances 343
Naphthalene - Methanal or Formaldehyde - Phenol - Resorcinol, Eosin and Fuchsin - Camphor, Menthol and Thymol - Turpentine and Terpene Hydrate - Oxalic Acid - Tannin or Tannic Acid - Picric Acid - Pyrogallic Acid - Tartaric Acid - Lactic Acid - Benzoic Acid - Salicylic Acid and Acetylsalicylic Acid - Indigo and Indigo Carmine - Aniline - Hydroquinone - Albumin - Thymol - Other Organic Substances - Chlorophyll and Colored Flowers
12.6 Some Unusual Experiments 363
12.7 Spectacular Reactions 366

12.8 Sources of Fire or Harmless Explosions 372

Chapter 13 - Photochemical Reactions 381

Chapter 14 - Reactions on Heating in the Presence of at Least One Liquid

14.1 Reactions with Metals or Metalloids 383
Iron, Zinc, Copper, Tin, Lead - Magnesium and Aluminium - Chromium - Mercury - Cobalt and Titanium - Molybdenum - Vanadium - Tungsten - Bismuth - Antimony

14.2 Reactions with Nonmetals 390
Charcoal - Sulfur - Selenium - Phosphorus - Boron

14.3 Reactions with Halogens and Halides 395

14.4 Reactions with Mineral Acids or Mineral Salts 396
Mineral Acids - Sodium, Potassium, and Ammonium Salts - Iron, Zinc, and Nickel Salts - Copper Salts - Magnesium Salts - Lead and Tin Salts - Manganese Salts, Manganates and Permanganate - Chromium Salts and Chromates - Cobalt Salts - Molybdenum Salts - Titanium Salts - Vanadium Salts - Mercury, Silver, and Gold Salts - Antimony and Arsenic Salts - Other Salts

14.5 Reactions with Organic Substances 422
Acetic Acid - Oxalic Acid - Picric Acid - Tartaric Acid - Citric Acid - Butyric Acid - Tannin (Tannic or Gallotannic Acid) - Sucrose and Glucose - Phenol - Resorcinol - Formaldehyde (Formalin) - Thymol and Menthol - Urea - Naphthalene - Camphor - Aniline - Miscellaneous

Chapter 15 - Distillations and Other Similar Operations

15.1 Extractions 439
15.2 Distillations and Reflux Heating 440
15.3 Mixtures with Alcohols 442
15.3.1 Perfumed Esters 442
15.3.2 Other Esters 443
15.3.3 Preparation of Chloroform 447
15.4 Mixtures Without Alcohol 447
15.5 Extraction of Essential Oils 449
15.6 The Chemistry of Perfumes 450
15.7 Preparation of Chromyl Chloride and its Reactions 451

Chapter 16 - Heating Solids

16.1 Metals and Nonmetals 455
Sodium - Iron - Copper - Zinc - Lead, Tin - Magnesium - Aluminium - Chromium, Titanium, Tungsten, Molybdenum - Cadmium - Mercury - Antimony - Carbon - Sulfur and Selenium - Phosphorus

16.2 Various Mineral Acids and Salts 472
With Mineral Acids - With Sodium, Potassium, Ammonium, and Calcium Salts - With Iron, Zinc, Copper, Nickel, and Lead Salts - With Magnesium Salts - With Manganese Salts - With Chromium Salts - With Antimony and Arsenic Salts - Vanadium Salts and Vanadates - With Salts of Other Metals

16.3 Various Organic Substances 482

Chapter 17 - Electrochemistry and Physics Experiments

17.1 Electrochemistry 485

17.2 Three Physics Experiments 487

Chapter 18 - Cleaning Laboratory Glassware 489

Table of Nearly 120 Analytical Experiments 492

ADDENDUM

1 - How to Measure Temperatures 495
2 - Baumé Degrees 496
3 - How to Bend Glass Tubing 497
4 - Building a Cooling Circuit or Water Aspirator That Uses Very Little Water 498
5 - Cooling Mixtures 498
6 - Choice of Crucibles 499
7 - Two Books 500

This page intentionally left blank

PREFACE

I was not yet thirteen years old when, by a fortunate chance, I came across an old chemistry book. The illustrations fascinated me. They showed assemblies of apparatus that seemed mysterious to me and reminded me somewhat of the lair of a mad scientist, like those sometimes seen in comic books or movies. I spent a long time absorbed in that book, reading and rereading the texts almost at random in an effort to understand those that seemed the simplest. Through perseverance, even though I had not yet taken a single chemistry class at school, I gradually came to understand the experiments, progressing from the simplest to the most complex. Moreover, that chemistry book used an outdated nomenclature, something that later proved useful when I began reading books even older than that one.

I then felt the desire to perform experiments myself. My family, knowing me to be cautious and prudent, accepted the idea and helped me. I will never forget my very first Erlenmeyer flask and those few simple experiments that I first carried out in the kitchen or in the garden. Later, I was given a room, furnished with a few old pieces of furniture, and supplied with gas since running water and a sink were already available there.

I then bought my first recently published chemistry book and, after my mother and I had written to the publisher, I was able to establish contact with a glassblower in my region who also happened to be a subcontractor for Prolabo, then a subsidiary of Rhône-Poulenc (France).

I realized very early that chemistry would never become my profession but would always remain a fascinating hobby. Although I loved watching certain substances transform before my eyes, the mathematical aspects of the science held little appeal for me. At the age of eighteen, after I had already acquired quite a collection of equipment and chemicals, I was forced to give up my practical experiments because my teacher training demanded too much of my time. I nevertheless continued taking notes from books consulted in a public library. This interruption lasted much longer than I had wished, for shortly after completing my

studies and finding employment, I got married and built a house, already setting aside space for a future laboratory. Once it had been installed, I was able to resume my experiments, very often observed or assisted by a wonderful wife who was every bit as interested and fascinated as I was.

The years passed, and I retired not long after the glassblower who had welcomed me so warmly when I was just beginning.

Today, when I look back, I realize that I have traveled a long and fascinating path in chemistry. And I believe the time has come to allow others to benefit from the knowledge—and above all the practical know-how—that I have acquired in this field through more than half a century of laboratory practice.

Let there be no misunderstanding: I have in no way intended to write a chemistry textbook. I have simply wanted to place in their hands a kind of laboratory companion capable of stimulating their scientific curiosity and serving as a practical guide for safe experimentation.

INTRODUCTION

Because of budget cuts and increasingly stringent regulations governing the use of certain chemical substances now regarded as hazardous, difficult to handle, or inappropriate for general possession, secondary-school chemistry teachers have gradually been forced to reduce the number of experiments performed in the classroom. In some cases, practical demonstrations have disappeared altogether. In others, students must now be content with watching a few videos or carrying out experiments so unremarkable that they are unlikely to spark any real enthusiasm.

As a result, an increasing number of students now regard chemistry as an abstract science, much like mathematics. Meanwhile, a small minority turn to the Internet—especially YouTube—in search of scattered pieces of information, which they sometimes use as the basis for attempting impressive experiments on their own. Unfortunately, many of these demonstrations are presented by individuals with limited experience or inadequate equipment. The risks and disappointments that can result from such an approach are easy to imagine.

This volume seeks to provide clear and reliable guidance on the experimental aspects of chemistry. It is intended first and foremost for amateur chemists who wish to perform interesting experiments at home without endangering their health, their safety, or their property. It is also aimed at teachers looking for ideas that will make their lessons more engaging, since many of the experiments described here can be adapted both to the equipment available in schools and to the safety regulations that govern school laboratory activities.

This is by no means a conventional chemistry textbook. It is a PRACTICAL LABORATORY GUIDE organized around a purely practical approach. Theoretical discussions have deliberately been kept to a minimum, and neither its chapters nor their contents follow the sequence traditionally imposed by academic chemistry courses or school curricula. Instead, its chapters are arranged in a logical sequence based on practical work rather than on theory. Its sole ambition is to introduce readers to a science whose experimental dimension has all too often been

overshadowed in modern textbooks by an emphasis on theory.

Chemistry is not a game. It should never be approached carelessly, without adequate knowledge, or through improvisation. The best way to learn chemistry is to begin with simple experiments before progressing to increasingly demanding procedures requiring more sophisticated equipment. This principle has guided the way the experiments in this book have been organized. They have also been grouped according to the relative ease with which the necessary chemicals can be obtained by an amateur experimenter. The overall structure of the book is therefore designed to answer, as quickly as possible, a simple practical question: "Which experiments can I perform with the equipment and chemicals I already have?"

Organic chemistry experiments are generally less colourful than those of inorganic chemistry and are therefore often considered less attractive to beginners. Moreover, inorganic chemistry is rightly regarded as the essential foundation upon which all other branches of chemistry are built. For these reasons, the present guide focuses primarily on experiments in inorganic chemistry.

I have said that this book is intended chiefly for amateur chemists. This does not mean people entirely lacking in basic scientific knowledge or common sense. Beginners will certainly find many stimulating experimental ideas in the pages that follow, but I nevertheless strongly recommend that they read the entire first chapter with great care. It deals with a number of essential topics concerning the organization of the laboratory and the proper use of laboratory equipment—knowledge that every experimenter should master before attempting any practical work.

I am well aware that some professional chemists will object to the inclusion of certain substances described in this book, arguing that they are too hazardous to be owned or handled by amateur experimenters and therefore belong exclusively in specialized laboratories or industrial facilities. My answer is that such reasoning is not very different from the attitude some adults adopt toward sex education. The simple truth is that it is often far more irresponsible to ignore certain subjects—or to discourage people from learning about them—than to answer honest questions openly as they naturally arise. Intellectual curiosity is never inappropriate. On the contrary, it is the very foundation of learning. When curiosity is met only with prohibition or embarrassment, it all too often drives people to seek information from sources that are incomplete, unreliable, or simply incorrect, exposing them to dangers they may not even realize exist. It is therefore always preferable to discuss openly the subjects that interest them and to explain clearly which experiments they can safely perform, while providing all the knowledge they need to avoid mistakes whose consequences can sometimes be disastrous.

CONFUSIONS, IMPRECISIONS, AND ERRORS

Confusions

Over the centuries, the terminology used to describe chemical substances has undergone profound changes. Chemists have gradually replaced many traditional names with terms based on increasingly systematic and sophisticated classifications. This has undoubtedly been beneficial for professionals, but not necessarily for non-specialists.

For example, although ethanoic acid is scientifically more precise than acetic acid, the latter immediately evokes vinegar and its characteristic smell for the beginner. Likewise, terms such as dihydrogen, dichlorine, dibromine, and diiodine may confuse readers who are perfectly familiar with hydrogen, chlorine, bromine, and iodine without feeling the need to distinguish so rigorously between an element and its molecular form.

Unfortunately, this evolution in chemical terminology did not occur overnight. Over the years, many substances have been known by a succession of different—and sometimes confusingly similar—names. Few examples illustrate this better than the term magnesia. To athletes, magnesia refers to a particular form of magnesium carbonate used to keep the hands dry and improve grip. Pharmacists, however, have long used expressions such as heavy magnesia, light magnesia, calcined magnesia, liquid magnesia, and milk of magnesia to designate a variety of substances, including magnesium oxide, magnesium hydroxide, and even magnesium bicarbonate. Small wonder that the non-specialist can easily lose his way in this maze of pharmaceutical terminology.

To make matters even more confusing, many traditional names based on historical methods of manufacture are still widely used by the general public. Thus, one may still hear oil of vitriol used for sulfuric acid, while hydrochloric acid is sometimes referred to as spirit of salt or even muriatic acid.

To avoid confusing amateur chemists, I have chosen throughout this book to use the names by which most substances are commonly known. Experienced chemists will have no difficulty, should they wish to do so, in mentally replacing these familiar names with more systematic terminology—for example, substituting hydrogen chloride for hydrochloric acid whenever greater precision is required.

Because chemistry is now taught in an increasingly theoretical manner, its fundamental concepts are often only superficially understood and are therefore quickly forgotten. This gives rise to a surprising number of widespread misconceptions.

Many people, for example, confuse chlorine with household bleach, or even with hydrochloric acid. I once read a newspaper report claiming that hydrochloric acid had leaked into a swimming pool! In March 2017, the Belgian press reported that a leak of nitric acid had occurred in the village of Zevekote and had produced a huge yellow cloud. In reality, the leak involved nitrogen dioxide—a completely different substance with entirely different properties and hazards.

Confusion also frequently arises between ammonia and aqueous ammonia, the first being the gas and the second its solution in water. Detective novels are also prone to perpetuating a widespread misconception: they almost invariably confuse arsenic, which is in fact a chemical element (As), with arsenic trioxide (As_2O_3)—formerly known as arsenious oxide—a highly toxic compound. This substance, now prohibited for such purposes, was once sold—often mixed with thallium salts, which are also highly toxic—under the generic name rat poison.

Imprecisions

Nothing is more embarrassing for a chemistry teacher than seeing an experiment fail in front of amused students, and nothing is more frustrating for an amateur chemist than being unable to reproduce the results described in what appeared to be a reliable chemistry book.

Why does an experiment sometimes fail completely, proceed in an unexpected manner, or even suddenly become uncontrollable, leading to broken apparatus—or worse, personal injury?

A chemical reaction is always influenced by several factors. The first that every beginner quickly learns to appreciate is temperature. Those whose importance is most often underestimated—indeed, frequently overlooked altogether—are pressure, the nature of the light, and its intensity. Yet there is another factor that is just as essential: the concentration and purity of the substances involved.

Some experiments simply fail, or produce unexpected results, because the chemicals

employed are impure. Impurities may already be present when a product is purchased, particularly if it is intended for industrial or hardware-store use, but they may also result from improper storage. The opposite situation may also occur: no reaction takes place because the substances are excessively pure, as is the case with certain metals that fail to react with acids under such conditions.

One important point to remember is that even a slight change in the concentration of the reactants may profoundly alter the outcome of an experiment. Whenever an experiment fails to produce the expected result, one should never hesitate to repeat it while modifying, one at a time, the concentration of each reagent involved.

Many other factors, however, can also lead to disappointment...

I have practised chemistry as a passionate amateur for more than half a century. Throughout those years, I constantly searched through books and scientific publications by respected authors in the hope of finding the most accurate descriptions possible of both simple and complex experiments. To my great surprise, I gradually discovered that omissions, imprecisions, contradictions, and even outright errors are far more common in the chemical literature than one might expect.

The most frequent omission is the failure to mention that heating is required in order to obtain the expected result. Another concerns the duration of an experiment, a point that is often left entirely unspecified. Amateur chemists unfortunately tend to assume that the reactions described by an author—or represented by a chemical equation—occur immediately. In reality, some reactions require many minutes, several hours, or even entire days before producing their full effect.

OBSERVE CAREFULLY AND BE PATIENT

One mistake frequently made by experimenters is to shake or stir their reaction vessels as soon as potentially reactive substances are brought together. In many cases, it is far better first to observe carefully and resist the temptation to intervene too quickly.

By observing closely, one may notice phenomena that would otherwise go unnoticed. A precipitate, for example, may pass through a succession of colours before finally acquiring a uniform appearance. Such observations can sometimes provide valuable information about the course of a reaction.

Another common mistake is to discard the products of a reaction too soon, without allowing sufficient time for further changes to occur. Many chemical reactions continue to evolve long after the initial mixing of the reagents. Significant changes may appear after a few minutes, several hours, a number of days, or even longer. Indeed, some scientific discoveries originated from reaction vessels that had simply been forgotten on a laboratory shelf and later re-examined.

It is worth pointing out that modern readers are often unaware that, in Lavoisier's time, balances and other measuring instruments were far less precise than those available today. Obtaining accurate results therefore required experiments to be carried out on relatively large quantities of material and repeated many times in order to obtain average values that approached a reasonably accurate result.

Many modern educational chemistry books state that Lavoisier merely heated mercury in contact with air and obtained red mercury oxide, whose mass exceeded that of the original mercury. They then explain that, after sealing the liquid metal in a flask connected to a mercury trough, he observed that the total mass of the apparatus remained unchanged. From this, he concluded that the increase in mass observed during the first experiment resulted from the combination of mercury with oxygen from the air.

Presented in this way, the experiment appears both simple and quick to perform. However, if one consults Lavoisier's own publications rather than these modern summaries, a rather different picture emerges. We learn that he had to maintain the heating for twelve days and that the first tiny red spot of oxide appeared on the surface of the mercury only on the second day. This is precisely the kind of "minor detail" whose omission can seriously mislead anyone attempting to reproduce this historic experiment.

Beyond the omissions just discussed, chemical literature contains many examples of imprecision and contradiction.

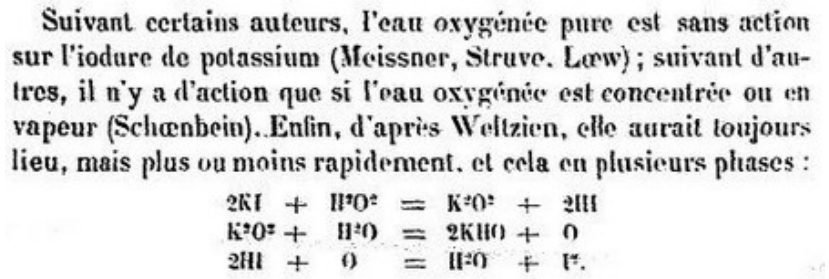
In a collective work such as the famous *Dictionnaire de chimie* by Wurtz which despite its age remains an important reference, one frequently encounters statements of the form: "So-and-so states that..., whereas another author states that..." Given the importance of such a work, is it not surprising that no one took the trouble to determine which author was correct?

Some readers may assume that these discrepancies were undoubtedly resolved long ago. Unfortunately, that is not necessarily the case. One might even argue that contradictions multiplied over time.

The monumental *Comprehensive Treatise on Inorganic and Theoretical Chemistry* by J. W. Mellor, published in London in sixteen volumes between 1922 and 1937, contains countless examples of contradictory observations reported by different chemists concerning reactions that should, in principle, have produced identical results.

Even more striking is the monumental *Traité de chimie minérale*, first published under the direction of Paul Pascal between the two World Wars and reissued several times until the 1960s. It is not uncommon to find, in the descriptions of physical properties, several different boiling points reported for the same substance.

Another example may be found on page 258 of the first volume of *Traité de chimie minérale et organique* by Wilm and Hanriot (Paris, Masson, 1888), where one encounters the following statement:



Suivant certains auteurs, l'eau oxygénée pure est sans action sur l'iodure de potassium (Meissner, Struve, Lœw) ; suivant d'autres, il n'y a d'action que si l'eau oxygénée est concentrée ou en vapeur (Schœnbein). Enfin, d'après Weltzien, elle aurait toujours lieu, mais plus ou moins rapidement, et cela en plusieurs phases :

$$2KI + H^2O^2 = K^2O^2 + 2HI$$
$$K^2O^2 + H^2O = 2KHO + O$$
$$2HI + O = H^2O + I^2.$$

Translation :

> According to some authors, pure hydrogen peroxide has no effect on potassium iodide (Meissner, Struve, Loew); according to others, it acts only when concentrated or in the form of vapor (Schœnbein). Finally, according to Weltzien, the reaction always takes place, although more or less rapidly, and proceeds in several stages:

One cannot help being surprised by the lack of scientific curiosity displayed by these two university professors, who were content to repeat the claims of others without attempting to verify them, even though doing so would have been quite straightforward.

Today, this very simple experiment continues to surprise many people who encounter it on the Internet under the rather amusing name of "elephant toothpaste." The spectacular foam jet produced by the reaction does indeed resemble an enormous quantity of toothpaste being squeezed from a tube in a single burst. How, then, could chemists have claimed that hydrogen peroxide had no effect on potassium iodide?

In their desire to simplify chemistry for educational purposes, some authors have occasionally provided explanations that are, quite frankly, absurd.

The following examples are taken from *Cours élémentaire de chimie* by A. Maillard (Paris, De Gigord, 1921) and *Leçons élémentaires de chimie* by Berthe Bussard and Hélène Dubois (Paris, Belin, 1897).

In order to explain how Lavoisier demonstrated that diamonds are composed of carbon by analysing the gases produced during their combustion beneath a bell jar, the authors merely stated that he used a lens. They even illustrated it as though it were nothing more than an ordinary magnifying glass (Illustration 1). Try, however, to burn a diamond with a simple magnifying glass!

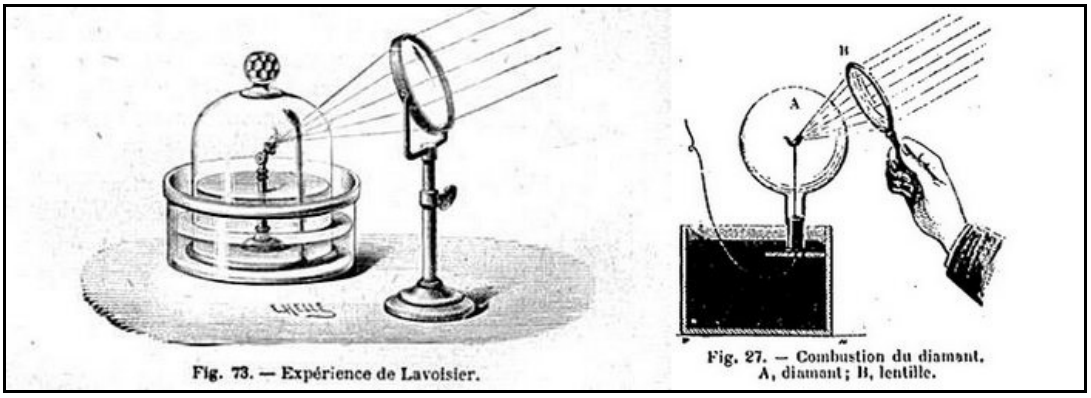


Illustration 1

In reality, Lavoisier employed an enormous lens known as the Palais-Royal Lens. This remarkable instrument, which he borrowed from the French Academy of Sciences and which was housed at the Palais-Royal in Paris, had been manufactured from exceptionally clear glass by the renowned scientist and craftsman Ehrenfried Walther von Tschirnhaus, a master in this field. Had the three authors mentioned above been more rigorous, they might also have pointed out that Lavoisier carried out several different experiments before he was able to construct a complete demonstration.

This is an appropriate place to mention the fascinating article written by Josette Fournier concerning Lavoisier's experiments on the composition of air. Easily found online, this study shows that numerous famous chemists, when recounting this landmark experiment, departed so far from the historical reality that one is tempted to conclude that they never performed the experiment themselves—and may even have copied inaccurately what previous authors had written.

Let us now turn to actual errors.

Errors

The most common and least serious ones may simply result from an author's momentary lapse of attention, or from mistakes introduced during the preparation and printing of a book.

For example, in Paul Remy-Genneté's *700 Expériences de cours de chimie* (Paris, Presses Universitaires de France, 1962), one finds on page 499, a description of an experiment involving nothing more than magnesium chloride and hydrochloric acid. Yet the author states that the reaction produces... ammonium chloride!

A little further on, page 526 contains a diagram illustrating the combustion of aluminium powder, but one of the arrows identifies the metal involved as "Mg". Such

mistakes, I should add, can happen to anyone—even to me. This is why one can never be too careful when proofreading a manuscript, preparing a book for publication, or indeed when reading one.

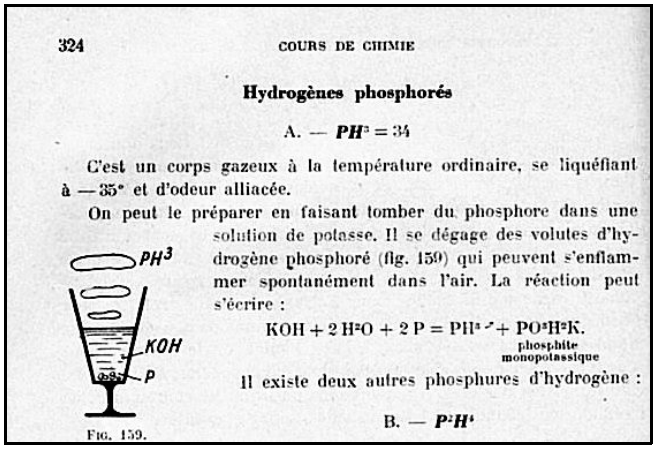
But let us consider a rather different case.

In 1909, on page 109 of his book *Chemical Lecture Experiments* (New York, Macmillan Company), the chemist Francis G. Benedict explained that hydrobromic acid could be prepared by heating potassium bromide with dilute sulfuric acid (three volumes of concentrated acid mixed with one volume of water). He further stated that the small amount of bromine evolved together with the hydrogen bromide could easily be removed by passing the gas through a U-tube containing red phosphorus. At first sight, this appears to be a simple and convenient method for preparing hydrogen bromide gas. Unfortunately, as early as 1861, the chemist Regnault had already pointed out the shortcomings of this procedure in his *Premiers éléments de chimie* (Paris, Masson et Garnier). When sulfuric acid reacts with potassium bromide, substantial quantities of bromine are produced, but also sulfur dioxide (SO_2), which is far from easy to separate from the desired gas. The amount of bromine generated may even be sufficient to ignite the red phosphorus contained in the U-tube. Furthermore, it is not dilute sulfuric acid that should be used, but concentrated sulfuric acid. A dilute acid would immediately dissolve the hydrogen bromide, which is highly soluble in water, thereby greatly reducing—or even completely preventing—its evolution. One is therefore entitled to wonder whether Benedict ever actually used the method he recommended.

Comparing the descriptions of the same experiment given by different authors sometimes reveals that some merely copied, word for word, what a predecessor had written, without even acknowledging the source. Such behaviour is nothing less than straightforward plagiarism.

Other authors, without truly plagiarising, appear at times to have relied upon vague memories of what they had read in books when describing experiments that they had quite obviously never performed themselves.

Thus, in *Cours de chimie à l'usage des candidats aux concours administratifs et techniques* by Professor Balloul (Paris, Librairie de l'Enseignement Technique, 1935), one may read on page 324 (Illustration 2) that it is sufficient to drop phosphorus into a solution of potassium hydroxide in order to produce phosphine (PH_3), which supposedly escapes from the liquid in swirling clouds. Not only does the


324 COURS DE CHIMIE

Hydrogènes phosphorés

A. — $PH^3 = 34$

C'est un corps gazeux à la température ordinaire, se liquéfiant à — 35° et d'odeur alliacée.

On peut le préparer en faisant tomber du phosphore dans une solution de potasse. Il se dégage des volutes d'hydrogène phosphoré (fig. 159) qui peuvent s'enflammer spontanément dans l'air. La réaction peut s'écrire :

$$KOH + 2\,H^2O + 2\,P = PH^3 + PO^2H^2K.$$

phosphite monopotassique

Il existe deux autres phosphures d'hydrogène :

B. — P^2H^4

PH3
KOH
P
FIG. 159.

Illustration 2

author fail to specify the essential point—whether the phosphorus is red or yellow—but the accompanying illustration, showing nothing more than a stemmed laboratory glass, confirms a major flaw in the experimental description: the reaction produces the stated result only when the substances are heated together, and only if the phosphine generated is prevented from coming immediately into contact with the atmosphere, since it ignites spontaneously in air.

Here is another instructive example, this time taken from the second volume of a pedagogical work simply entitled *Chimie* (Liège, Librairie Sciences et Lettres, 1953), written by Robert Petit, Doctor of Chemical Sciences and teacher.

On page 285 of this book appears a rather complex experimental diagram (Illustration 3).

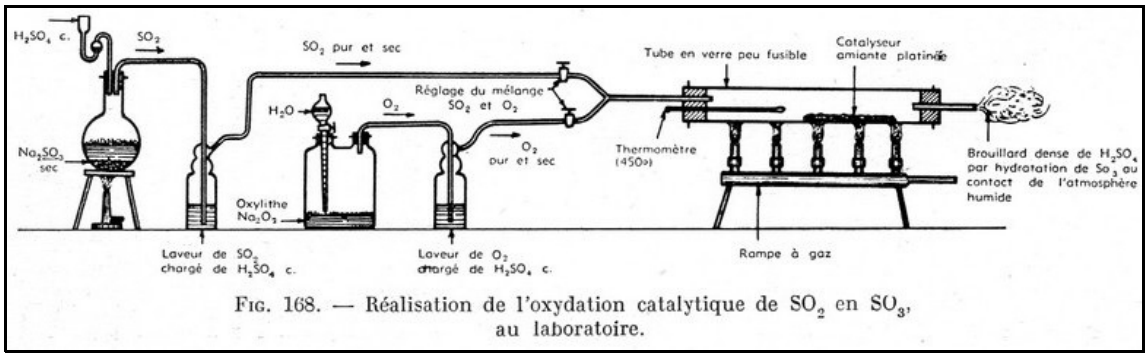


FIG. 168. — Réalisation de l'oxydation catalytique de SO_2 en SO_3, au laboratoire.

Illustration 3

The flask on the left is said to contain "dry" sodium sulfite. Yet the drawing clearly shows the sulfite covered by a substantial layer of liquid. Let us assume that this liquid is the sulfuric acid introduced through the addition funnel above. Even so, two serious problems immediately arise. First, the reaction proceeds at room temperature, making the presence of a Bunsen burner beneath the flask entirely inappropriate. Second, when sulfuric acid is poured onto dry sodium sulfite, sulfur dioxide is indeed evolved, but a crust rapidly forms around the solid, preventing the reaction from continuing. No matter how much additional acid is added, as suggested by the diagram, the reaction soon comes almost to a halt. Later in this book, the reader will learn how this difficulty can be avoided. At the centre of the diagram are two stopcocks, identified by arrows bearing the label: "Adjustment of the SO_2/O_2 mixture." Let us imagine for a moment that the stopcock located on the sulfur dioxide inlet is closed, even slightly. An overpressure would immediately develop in the reaction flask—and in the wash bottle connected to it. As a result, the sulfur dioxide would seek another escape route and would be forced back through the so-called safety funnel used to introduce the sulfuric acid. The acid contained in the bend of that funnel would then be projected outward. Now imagine the opposite situation, in which the oxygen stopcock is partially closed. Since the reaction flask itself is tightly sealed by a stoppered addition funnel, the resulting overpressure would most likely force out the stopper of the wash bottle, which is the least securely fastened component of the entire apparatus. So many errors accumulated

in a single diagram clearly demonstrate that the author never carried out the experiment in the manner depicted. Furthermore, since even a professional illustrator could not have produced such a diagram without first working from a sketch supplied by the author, these mistakes must ultimately originate with the author himself.

The same book also contains, on several occasions, a diagram like the one shown opposite (Illustration 4). Yet it is obvious that if the top of the test tube is sealed with a stopper while a gas is supposed to enter it, this simply cannot work. Either the stopper will be blown out, or something similar will occur at the gas generator itself.

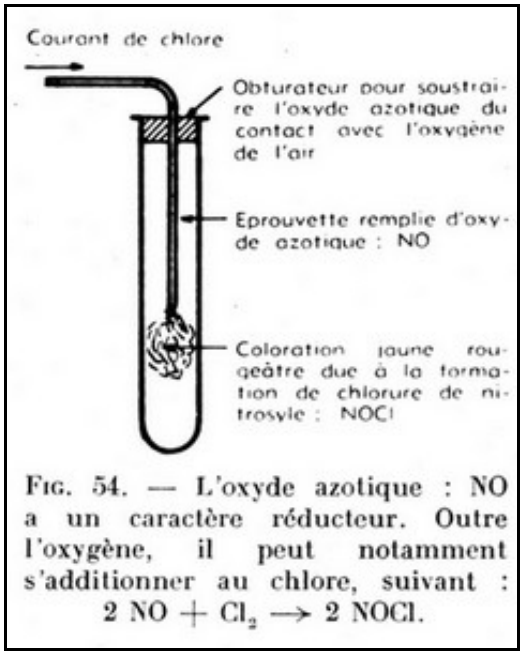

Courant de chlore
Obturateur pour soustraire l'oxyde azotique du contact avec l'oxygène de l'air
Eprouvette remplie d'oxyde azotique : NO
Coloration jaune rougeâtre due à la formation de chlorure de nitrosyle : NOCl

FIG. 54. — L'oxyde azotique : NO a un caractère réducteur. Outre l'oxygène, il peut notamment s'additionner au chlore, suivant : $2\ NO + Cl_2 \longrightarrow 2\ NOCl$.

Illustration 4

Another equally instructive example may be found on page 128 of the book by Paul Remy-Genneté mentioned earlier. The author states that it is sufficient to pour milk of lime into a flask filled with chlorine and then shake the vessel to see the greenish-yellow colour of the chlorine disappear and the flask adhere to the palm of the hand because of the partial vacuum created inside. Up to this point, the description is perfectly correct. The author then goes on to claim that adding a small quantity of hydrochloric acid will cause the colour of the chlorine to reappear. In reality, this belongs more to the realm of imagination than of experimental chemistry. Upon adding hydrochloric acid, the acid will react not only with the chlorine compounds present but also with the lime itself, producing colourless carbon dioxide. Mixed with whatever chlorine may be liberated, this carbon dioxide makes the chlorine virtually invisible. The author appears, in fact, to have unconsciously merged two entirely different experiments. The second consists of adding acid to a substantial quantity of bleaching powder, either dry or mixed with a small amount of water.

Before concluding the many observations and remarks contained in this introductory chapter, I should like to draw attention to one final aspect of the chemical literature...

Over time, our understanding of the ecological and physiological effects of chemical substances has continued to evolve and become more refined. Many compounds once used in medicine have subsequently been abandoned after their harmful effects became apparent in the short or medium term—effects that had not been recognized when those substances were first introduced. Increasing caution has likewise become the rule in chemical laboratories with regard to the handling of chemicals.

In chemistry treatises published before the Second World War, it was not uncommon to find comments concerning the taste of various chemical substances. Such remarks clearly imply that those substances had actually been tasted—a practice that was, to say the least, dangerous and, from a modern perspective, quite astonishing.

But there is an even more striking example. In his book *Manipulations de chimie – Métalloïdes*, published in Paris by Dupont in 1899, the chemist Mermet could still write, on page 750: "Borax does not appear to be harmful to humans, who may absorb from 5 to 15 grams or more per day without ill effect. The same does not seem to be true of plants, however, since even a dilute solution of boric acid rapidly kills them." Yet although borax and its derivatives were long used in pharmacy as disinfectants and as additives in cleaning products, we now know that even at relatively low doses they are sufficiently toxic to reproductive organs that their sale is strictly regulated and, in principle, prohibited to private individuals in many jurisdictions.

Before using any chemical substance, amateur chemists would therefore be wise to consult reliable toxicological and safety references. Among the most useful English-language sources are the *Safety Data Sheets* (SDS) supplied by chemical manufacturers, the publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), and *The Merck Index*, long regarded as one of the most authoritative reference works on chemicals, drugs, and biological substances. French-speaking readers may also consult the toxicological data sheets published by the INRS (Institut National de Recherche et de Sécurité pour la prévention des accidents du travail et des maladies professionnelles, France) and the CNESST (Commission des normes, de l'équité, de la santé et de la sécurité du travail, Canada). The European Chemicals Agency (ECHA) also provides valuable information concerning the European REACH regulations, which now govern many aspects of the marketing, transport, and use of chemical substances throughout Europe. Admittedly, however, this regulatory framework can sometimes resemble a maze in which even experienced readers may easily lose their way.

WARNING

Never improvise chemical mixtures or reactions. Chemistry is an exact science that deserves to be approached with seriousness and discipline. It is not an art in which anyone is free to mix substances at random, any more than an amateur painter would indiscriminately blend pigments simply to see what new colours might appear.

Chapter 1 - Laboratory Equipment

1.1 Laboratory Layout and Workspace Design

Unlike a teacher, who generally has to make do with whatever equipment the school administration provides, the amateur chemist setting up a personal laboratory is free to decide what equipment is necessary or sufficient. One principle should never be forgotten: quality must never be sacrificed for quantity. Fragile or poorly suited equipment is an obvious source of danger.

The room in which chemical experiments are carried out should be large enough to allow comfortable movement. A cramped working area inevitably increases the risk of knocking over bottles, apparatus, or chemicals.

The laboratory bench is the piece of furniture on which most experimental work is performed. It should be sturdy and stable. Its working surface must be flat, level, and as resistant as possible to flames, heat, and corrosive chemicals. A tiled surface is therefore preferable, although glass and certain plastics may also be acceptable despite their obvious limitations. Wooden surfaces should be avoided, and metal worktops should be ruled out altogether.

The bench will normally be accompanied by a sink intended primarily for cleaning glassware. A plastic sink is generally preferable to a porcelain one, as it reduces the likelihood of breakage during washing. The basin should be wide and deep enough to accommodate relatively large vessels. Above it should be one or more water taps fitted with stepped hose connectors, allowing flexible tubing to be attached easily. A laboratory drying rack, equipped with numerous pegs for supporting glassware, should be firmly mounted nearby. This rack may be made of plastic or of metal protected by a plastic coating.

One or more safety electrical outlets should be located within easy reach of the bench.

Good general ventilation is essential. This may be provided by a skylight or by a window, provided that neither opens directly onto a neighbour's property or a frequently used pedestrian area. Better still is a door located close to the bench and opening onto a garden or similar outdoor space, as this also provides a rapid means of evacuation should an emergency arise. A powerful wall-mounted extractor fan can be a valuable addition for removing fumes that might otherwise accumulate in the laboratory. Professional laboratories often employ fume cupboards designed specifically for extracting hazardous gases and vapours. Such installations are generally beyond the financial reach of amateur chemists. They cannot simply be replaced by domestic or commercial kitchen hoods, since corrosive gases such as chlorine or hydrogen chloride would quickly damage them. Nevertheless, gases leaving the final vessel of an apparatus can easily be discharged through a PVC tube connected to a glass outlet passing through an exterior wall and venting outdoors, well away from areas used by people, animals or plants. Whenever possible, however, gases should first be passed through a suitable liquid capable of absorbing or neutralising them before any release to the atmosphere is considered. Chemical waste should likewise be stored and disposed of in accordance with sound environmental practice and appropriate safety precautions.

Glassware, electrical equipment, and chemical reagents should be stored in robust cabinets securely fastened to the walls and capable of remaining closed even under extreme circumstances. Wherever possible, chemicals should not be kept on open shelving. If this cannot be avoided, they should be arranged so that a fall and breakage could not lead to a serious accident. Highly corrosive substances and flammable solvents should always be stored as close to floor level as practicable. Chemicals should not all be stored together. Storing chemicals in separate rooms or clearly segregated storage areas greatly reduces the risk of dangerous reactions should containers break. Similar precautions apply to highly flammable or potentially explosive materials. These recommendations are largely matters of common sense, but they are worth repeating nonetheless.

Storage areas must be permanently ventilated to prevent the accumulation of toxic or explosive vapours. They should be kept cool, whereas the laboratory itself should remain comfortable without becoming excessively warm or cold.

The quantities of chemicals stored should always reflect actual needs. There is little risk in keeping a generous supply of demineralised water, but maintaining large stocks of flammable, explosive, or highly corrosive substances is both unnecessary and hazardous.

During experimental work, neither ventilation nor vapour extraction alone is sufficient to eliminate all risks of poisoning or explosion. Basic safety rules must also be observed. For example, in the presence of an open flame or a significant heat source, a bottle containing a highly flammable liquid should never be opened unnecessarily or left uncapped. Particular caution is required when handling substances such as diethyl ether or carbon disulfide. Their vapours spread rapidly

beyond the container and form highly explosive mixtures with air. They also present serious physiological hazards, causing dizziness or drowsiness and, in the case of carbon disulfide, potentially severe poisoning that may even prove fatal.

When handling chemicals, especially during the early stages of learning laboratory techniques, it is advisable to wear thin but durable chemical-resistant gloves. Such gloves help protect against burns from acids and caustic substances while also reducing direct skin contact with carcinogenic or mutagenic compounds that may be absorbed through the skin. They do not, however, provide absolute protection. Careful handling remains essential whenever substances are transferred from one container to another. As a matter of good laboratory practice, any surface on which chemicals have been poured or transferred should be thoroughly washed with plenty of water at the end of each working day.

1.2 USEFUL EQUIPMENT

1.2.1 Laboratory Stands

The laboratory should include a number of metal support stands fitted with bases heavy enough to ensure good stability. The vertical rods may range in length from approximately 30 cm to 1 m and generally have a diameter of 10 or 12 mm, more rarely 16 mm or greater. Such stands are particularly useful for experiments carried out outdoors.

Within the laboratory itself, however, it is often preferable to install a permanent support framework occupying an area roughly one metre high by at least 1.2 metres wide rather than relying exclusively on individual stands. This framework should consist of a grid formed by horizontal and vertical metal rods, necessarily round in section and typically 12 or 16 mm in diameter, joined together by appropriate clamp connectors. The vertical rods should be permanently secured by clamping them into special base fittings, which are themselves firmly screwed to the laboratory bench. These fittings and connectors can be obtained from suppliers specialising in laboratory equipment or from companies dealing in certain types of commercial shelving and display systems. The rods themselves may be made of stainless steel, duralumin, or simply polished aluminium, which naturally develops a durable protective oxide layer over time. Suitable rods are available from specialist suppliers and many hardware stores. Ordinary steel should be avoided because it rusts rapidly, while copper tubing oxidises too readily for this purpose. A framework of this kind is capable of supporting virtually any laboratory assembly, including relatively heavy ones.

Some laboratory workers also appreciate portable support grids mounted between two heavy stands positioned at either end of an experimental setup. Common sense suggests, however, that such frameworks should remain of moderate

size—approximately 80 cm high and 1 m wide—so that they can be moved without undue difficulty, as they are inevitably rather heavy.

Glassware and apparatus are secured by means of a wide variety of clamps, rings, shelves, and supports specifically designed for laboratory use. These accessories are attached to the framework or to individual stands by means of suitable bossheads and connectors. They may be purchased from laboratory suppliers, obtained second-hand through specialist dealers, or occasionally found at scientific surplus sales and flea markets.

When assembling apparatus incorporating ground-glass joints, it is important not to overtighten every clamp. A small degree of flexibility should remain within the assembly so that stresses or vibrations generated during the reaction do not result in broken glassware. It is also highly advisable to place small strips of foam, silicone, or rubber between the glass surface and the jaws of any clamp holding a vessel. These strips act as shock absorbers and help protect the apparatus from vibration-induced damage.

Fifure 4

There is one final accessory that deserves a place in every laboratory: the laboratory jack, a metal lifting platform whose height can be adjusted precisely by means of a control screw. Laboratory jacks are available in various sizes, the smallest having a platform scarcely larger than a packet of cigarettes. Figure 4 shows a considerably larger model supporting a one-litre flask.

A laboratory jack is useful for supporting part of an apparatus, but its greatest value lies in conjunction with heating equipment such as electric heating mantles and sand, oil, or water baths. These devices retain considerable residual heat even after their gas or electrical supply has been switched off. By lowering the jack, the heat source can be moved away from the vessel almost instantaneously, thereby stopping the transfer of heat without delay. This can prove extremely valuable if a reaction begins to accelerate unexpectedly. Unfortunately, laboratory jacks remain relatively expensive pieces of equipment. The least costly models are not always the best choice, as they may be mechanically fragile and sometimes lack the precision required for safe work. In poorly made examples, the platform may even rise unevenly, making accurate adjustment difficult.

1.2.2 Common Laboratory Glassware

Laboratory glassware should always be of good quality. Particular caution is advisable when purchasing old glassware from flea markets, as it is often made from fragile glass that is poorly suited to modern heating methods. Similar reservations

apply to certain inexpensive modern products of Chinese or Indian origin whose walls may be excessively thin and therefore vulnerable to mechanical shock. I should add, however, that Chinese and Indian manufacturers have made remarkable progress in this field over the past twenty years, and some of their products can now compete with the finest European and Anglo-American laboratory glassware.

Modern laboratory apparatus is manufactured primarily from two types of glass: soda-lime glass, often referred to as laboratory glass, and borosilicate glass, sometimes incorrectly called Pyrex. Strictly speaking, Pyrex is not a type of glass but a registered trade name. Soda-lime glass is relatively fragile because it is highly sensitive to thermal shock. Nevertheless, it remains suitable for apparatus that is never heated, such as stemmed laboratory glasses, graduated cylinders with bases, or pipettes. Whenever possible, however, borosilicate glass should be preferred. It has become the standard material in modern laboratories because of its resistance to thermal shock, its chemical neutrality, and its mechanical strength.

The two best-known names associated with this type of glass are Pyrex and Schott/Duran. While the name Pyrex still generally denotes borosilicate glass of the 3.3 type, the situation is more complex with Schott/Duran, which now manufactures several hundred different glass compositions. Among these, the current Boro 3.3 closely corresponds to the former D50 grade, whereas G20, also known as Fiolax, is likewise a borosilicate glass but with less demanding performance characteristics. The quality of borosilicate glass depends largely on its coefficient of thermal expansion. The lower this value, the better the resistance to thermal shock. For high-quality borosilicate glass, the coefficient is approximately 3.3×10 K^{-1}. It is therefore important to consult catalogues carefully or to examine the permanent markings on the glassware itself before making a purchase. If no information is provided, caution is strongly advised.

A relatively recent technique makes it possible to apply a coloured surface treatment to borosilicate glass, rendering it actinic-resistant. Certain items are sold already treated in this way, while others can be modified afterwards by specialised firms, although the process is costly. Such glassware can often be recognised by slight variations in colour intensity, as the coating is rarely perfectly uniform. It should not be confused with conventional amber glass, whose colour is incorporated throughout the glass itself.

The principal types of laboratory glass are not always easy to distinguish visually. Traditional laboratory glass often displays an olive-green tint with yellowish undertones, whereas borosilicate glass may range from emerald green to an almost electric blue.

Even superior to borosilicate glass is fused silica, available in either transparent or opalescent form. In cross-section, a silica tube appears greyish white. Fused silica possesses an exceptionally low coefficient of expansion and therefore remarkable resistance to sudden temperature changes. A silica tube heated to red heat can, for

example, be plunged into cold water without damage. Yet silica is not without limitations. Like glass, it can be attacked by certain substances at elevated temperatures. Hydroxides, carbonates, carbon, vanadium, magnesium, and magnesium salts should never be strongly heated in silica vessels, as they rapidly damage the surface. Silica apparatus is also far less common than borosilicate glassware and is invariably more expensive. Furthermore, not all glassblowers are equipped to work with fused silica. Figure 5 shows, from left to right, the cross sections of a piece of ordinary laboratory glass tubing, a borosilicate 3.3 glass tube, and a fused silica tube.

Figure 5

Many complex assemblies are now constructed simply by joining together components fitted with standardised ground-glass joints. This was not always the case, as older joints lacked standardisation. To ensure gas-tight connections, some chemists use specialised greases, while others prefer a few drops of concentrated sulfuric acid. PTFE sleeves are also available commercially and are theoretically better suited to the task. Personally, however, I prefer the inexpensive PTFE tape commonly used by plumbers, which is available in a range of widths and thicknesses.

The vessels most frequently encountered in the laboratory are test tubes, flasks, erlenmeyer flasks, and beakers. Each deserves a brief description.

Beakers, whose name derives from a German word meaning a drinking vessel and which were once sometimes called Berlin vessels, are cylindrical containers available in either tall or low form. They may be fitted with a pouring spout and, in more recent designs, even with a handle. Although most are made of glass—occasionally actinic-resistant glass—they are also available in various plastics, PTFE, fused silica, stainless steel, and porcelain. Suitable for a wide range of operations performed either hot or cold, depending on the material, they have almost completely replaced the stemmed laboratory glasses formerly used in laboratories. Unlike those older vessels, beakers can generally be heated and stacked conveniently inside one another. Figure 6A shows, in the center, a stemmed glass, flanked by two beakers, one tall-form and the other low-form. Figure 6B shows

several special-purpose beakers: on the left, a beaker known as a saturation jar; in the center, a cylindrical beaker without a pouring spout; and on the right, a beaker fitted with an overflow device.

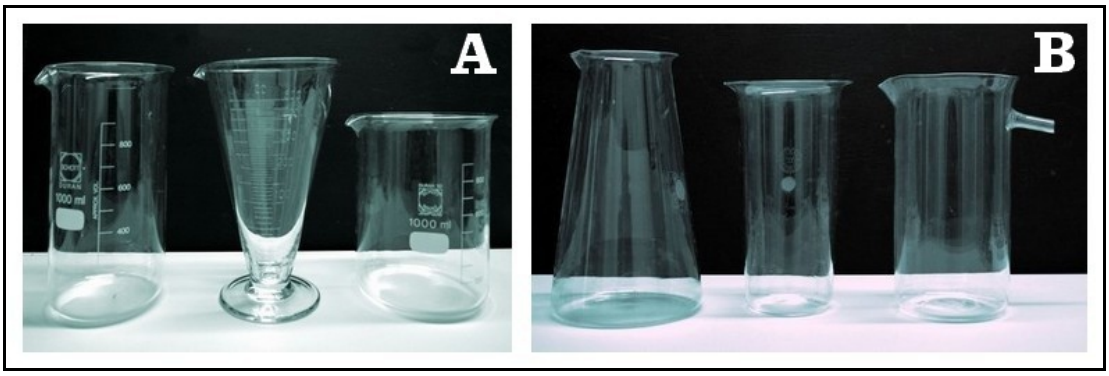


Figure 6

Flasks may be either round-bottomed or flat-bottomed and are available with wide or narrow necks, as well as short or long necks. Round-bottom flasks were once considered stronger than flat-bottom flasks and were therefore preferred. Modern manufacturing techniques have largely eliminated this difference. Round-bottom flasks nevertheless remain the preferred choice when electric heating mantles are used, since the heating chamber is almost always hemispherical. A flask is particularly well suited to reactions that may become vigorous or difficult to control. If initially filled to only one-third of its capacity, a boiling liquid can expand considerably within the body of the flask, increasing the surface area available for heat loss and thereby helping to delay or prevent overflow. Specialised forms of flask also exist, including distillation flasks, Kjeldahl flasks—named after the Danish chemist Johan Kjeldahl (1849–1900)—and pear-shaped flasks. A Kjeldahl flask is essentially a flask with a very long neck and an elongated body, whereas a pear-shaped flask tapers towards the bottom.

Erlenmeyer flasks, often referred to simply as erlens, take their name from the German chemist Emil Erlenmeyer (1825–1909), who designed them. They are conical vessels with a broad flat base narrowing progressively towards a relatively short neck, which may be either wide or narrow. They are convenient for rapidly heating liquids, but they possess one significant drawback: even a moderately vigorous reaction may overflow quickly because the narrowing walls restrict the expansion of the liquid surface.

One important variant is the filtering flask. Although identical in overall shape to a standard Erlenmeyer flask, it is fitted with a side arm located just below the neck. This side arm is normally connected to a vacuum source for filtration procedures, which will be discussed in a later chapter. Filtering flasks can also be useful for preparing gases. In such applications, a dropping funnel is fitted into the neck while the gas leaves through the side arm. Because filtering flasks are designed to withstand substantial vacuum, they are generally made from thick glass. For this reason, they should not be heated directly except in a water bath or sand bath. The

thicker the glass, the greater the internal stresses that may develop if heating is uneven, and these stresses can ultimately cause the vessel to shatter.

Apart from funnels and test tubes—whether straight-sided, flared, or pointed-bottomed, the latter being used primarily for centrifugation—it is worth examining a number of vessels designed for more specialised purposes.

The Woulff bottle appears to have been devised by the Irish chemist Peter Woulfe. Curiously, the name most commonly used today is not the exact spelling of his surname. Nevertheless, I shall continue to use the term Woulff bottle, as it remains the form most frequently encountered in chemical literature and among collectors of historical laboratory equipment.

Woulff bottles are cylindrical, flat-bottomed vessels fitted with several necks. Depending on the model, these necks may open through the top of the bottle—typically one to three necks—or through the lower part of the side wall, where a single neck is usually provided. Once extremely popular, these bottles, usually made from ordinary laboratory glass, have now been largely replaced by multi-neck flasks and, more recently, by specialised reaction vessels, although the latter are considerably more expensive. A particular variant of the Woulff bottle is sometimes referred to as a decanting bottle. Such vessels possess two openings, one at the top and another at the bottom, the lower opening usually being fitted with a stopcock. Large bottles of this type were formerly used as air aspirators: they were filled with water, and the gradual discharge of the water through the lower outlet created a stream of air entering through the upper neck. Similar vessels are still occasionally encountered in modern laboratories as storage bottles for distilled water or liquid reagents, which are then dispensed through the lower tap. Figure 7 shows several examples of Woulff bottles. At the rear left is a very old model fitted with two lower necks, a particu-larly uncommon arrangement. The remaining examples are more modern. The bottle at the front left and the one at the rear right may both be regarded as decanting bottles. The amber-glass example is considerably rarer than the colourless one. Woulff bottles have been manufactured in capacities ranging from approximately 100 mL to as much as 25 litres.

Figure 7

Drying devices for gases exist in many different forms. The simplest is, of course, an ordinary tube—sometimes even made of plastic—filled with a suitable drying agent. A more traditional design, now becoming increasingly uncommon in modern laboratories, is the drying column shown in Figure 8. This apparatus stands vertically on a broad base and incorporates a constriction located fairly low in the column, just above the lower side arm through which the gas enters.

Figure 8

The same purpose can also be served by U-shaped tubes, which may or may not be fitted with stopcocks. Such tubes are frequently used in electrolysis experiments, with an electrode placed in each arm of the tube.

Finally, mention should be made of the many varieties of gas-washing bottle, among which the Drechsel bottle is undoubtedly the best known (Figure 9). The principle was devised by Ferdinand H. E. Drechsel, from whom the apparatus takes its name. A Drechsel bottle consists of a vessel fitted with a hollow head carrying both a long inlet tube and a short outlet tube. The gas enters through the long tube, travels to the bottom of the bottle, bubbles through a liquid, and finally leaves through the shorter outlet tube located at the top.

The most sophisticated versions incorporate a gas-dispersing fritted-glass disc that produces much finer bubbles and therefore more efficient gas-liquid contact. Such a model can be seen on the left-hand side of Figure 9.

Figure 9

During the 1960s, the French manufacturer Sovirel introduced a rather costly variant in which the tubular head was adapted to Pyrex storage bottles originally intended for liquid reagents. The assembly employed a special screw cap known as an SVL closure, fitted with crown-shaped sealing rings. The immersion tube could slide vertically within the seal, allowing it to be adjusted to suit bottles of different capacities, usually 250 or 500 mL. Unfortunately, this very feature often compromised the seal, making the system less gas-tight than one might wish. While Sovirel-Pyrex bottles equipped with screw caps remain highly desirable for storing reagents—often more so than the ISO bottles discussed later—their Drechsel-bottle configuration cannot really be recommended. Another questionable design concept was later adopted by the Duran group, which added two additional plastic screw connections that were likewise incapable of providing a perfectly gas-tight seal. The central vessel shown in Illustration 9 represents a modified version in which the

imperfect screw-cap assembly has been replaced by a standard ground-glass joint. This adaptation allows the head to be fitted to a wide variety of vessels, including ordinary flasks.

1.2.3 Tubing

In experimental assemblies, it is not always possible to connect apparatus entirely by means of glass tubing. One may therefore use glass tubes joined together by short flexible connectors or, more commonly, flexible tubing connected to short glass tubes fitted, whenever possible, with hose nipples or olive-shaped ends. In the past, red rubber tubing—often referred to as English rubber tubing—was widely used. Although it remains remarkably practical, the modern tendency is to favour tubing made from PVC, translucent silicone, synthetic latex, or even PTFE. Each of these materials possesses its own advantages and disadvantages.

Rubber tubing resists many substances but eventually always becomes porous, either by turning brittle or by degrading into a sticky, gelatinous mass. Although clear PVC tubing is highly resistant to many chemicals, certain substances cause it to become opaque or to exude an oily material. Heat generated during a reaction may also soften and expand PVC tubing to the point where it can suddenly detach from the fitting to which it was connected, creating potentially serious hazards. Silicone tubing, which withstands heat and deformation better than PVC, may nevertheless become brittle or develop cracks, either with age or even during the course of a reaction. Like traditional English rubber tubing, it should therefore always be inspected before use by pulling on it gently. If the surface then shows signs of cracking, it should be discarded immediately. In any case, halogens should not be passed through silicone tubing; PVC tubing is preferable for such applications. PTFE tubing unfortunately remains relatively expensive and is generally available only from specialist suppliers. Contrary to what one might expect, it does not possess only advantages. Its flexibility is limited and its elasticity is virtually non-existent. Finally, tubing made from synthetic latex (elastomers) is extremely flexible and elastic but is likewise unsuitable for use with halogens and organic solvents.

The nature of flexible tubing is such that all types eventually age, more or less rapidly depending on the service conditions to which they are exposed. Consequently, they can be used only a limited number of times. There is, however, one exception. It is advisable to reserve two long lengths of English rubber tubing exclusively for connection to water-cooled condensers. Such tubing will last for many years provided it is hung up to dry after each use. The useful life of tubing may also be shortened by deposits that form during certain experiments. Such contamination should be monitored carefully, as it may give rise to unexpected reactions, including dangerous ones, or at the very least interfere with the outcome of subsequent experiments.

Older chemistry books are full of ingenious and practical devices devised by chemists who lacked the sophisticated equipment available today. In his small book *Pour le chimiste*, published in Paris by Dunod in 1934, the chemist Chaplet showed, for example, that a wide rubber tube cut in a simple manner could be transformed into the finest gripping tool imaginable—the human hand itself—allowing virtually any hot object to be handled without the risk of burns (see Figure 10). Today, such a device can easily be replaced by a simple sheet of silicone wrapped around the object to be grasped.

Figure 10

Many other silicone accessories originally designed for culinary use can likewise be adapted effectively for laboratory work. It cannot be emphasised strongly enough that the amateur chemist—and indeed many secondary-school chemistry teachers—must learn to be resourceful and to repurpose inexpensive everyday objects for laboratory use. To cite only a few examples, an aquarium made from synthetic material or the stainless-steel tank from a discarded deep fryer can serve as a water basin for collecting gases in various vessels; certain stainless-steel culinary cups can readily be converted into crucibles or beakers; small silicone moulds can serve as smalwater basins; and porcelain dishes can be used for small-scale reactions.

1.2.4 Stoppers

Two categories of stoppers must be considered. The first consists of solid, non-perforated stoppers whose purpose, as their name suggests, is simply to close bottles and other containers. The second consists of perforated stoppers, which are required for the construction of various types of experimental apparatus.

Apart from the screw caps originally supplied with bottles intended solely for storing chemicals, there are stoppers designed to close—often temporarily—vessels fitted with standardised ground-glass joints. This may be the case for graduated cylinders and volumetric flasks, but also for Erlenmeyer flasks, reaction flasks, and many other vessels whose contents the chemist wishes to preserve for later use. Such stoppers are made either of glass or of plastic. All are manufactured to fit precisely into the standard female joints for which they are intended. It is advisable to keep a complete assortment of different sizes, preferably stored in a compartmented box or drawer system where they can be organised conveniently and retrieved easily.

Some glass stoppers are hollow while others are solid. The solid versions are naturally heavier and are therefore better suited to vessels in which a slight internal overpressure may occasionally develop. Plastic stoppers, which are generally hollow, may have either perfectly smooth surfaces or a series of shallow raised rings. The latter design is particularly useful for liquids containing dissolved salts that might crystallise in the neck of the vessel and cause the stopper to become stuck.

Certain vessels are fitted with a male ground joint rather than a female one. For these, much rarer glass stoppers are available in the form of domes or hollow caps that fit over the joint. As a general rule, avoiding rare laboratory accessories is often the best way to avoid unnecessary expense.

Perforated stoppers, like flexible tubing, are indispensable components of many experimental assemblies. Whether intended for glass necks or for tubes made of glass, silica, ceramic, metal, or other materials, they are normally pierced with one or more cylindrical openings through which glass tubes may pass. Chemists of earlier generations relied chiefly on cork stoppers, which could easily be perforated using a cork borer. This tool consisted of a set of hollow tubes that fitted inside one another, each acting as a cylindrical cutting blade sharpened at one end. By rotating the selected tube while applying pressure, a cylindrical core of cork could be removed cleanly from the stopper. A traditional cork-borer set was usually accompanied by a sharpening tool resembling a double-bladed knife and designed specifically for maintaining the cutting edges of the borers. But cork stoppers suffered from two major disadvantages: they ignited easily and did not provide a truly satisfactory seal. As soon as better alternatives became available, they were therefore largely replaced by rubber stoppers.

Broadly speaking, two principal types of rubber stopper are encountered: red stoppers and grey-blue stoppers. The former are generally less flexible than the latter, which should therefore be preferred whenever possible. Laboratory suppliers offer pre-drilled rubber stoppers with anywhere from one to five holes, depending on the size of the stopper itself. Many years ago, Prolabo (France) marketed remarkable stoppers in which the holes were constricted only at their two extremities. This design prevented glass tubes from adhering to the stopper along their entire length after prolonged contact. Unfortunately, these excellent stoppers have now disappeared from the market. The only products now readily available are pre-drilled stoppers whose holes maintain the same diameter throughout their length. Modern designs do, however, offer one advantage over the old Prolabo models. The holes are only partially pre-drilled. At the base of each hole remains a thin membrane of rubber which, until pierced, ensures perfect sealing. Consequently, a stopper containing, for example, five pre-drilled holes may still be used as a solid stopper provided none of the membranes has been pierced by the user with a cork borer.

It is illusory to imagine that a perfectly cylindrical hole can easily be drilled through a rubber stopper using an ordinary drill and twist bit, no matter how sharp the latter may be. The result is invariably a torn and ragged opening. If one wishes to drill rubber stoppers personally, the proper approach is to use a vertical pillar drill fitted with standard laboratory cork borers serving as cutting tools. The real difficulty lies in holding the stopper securely without deforming it, thereby ensuring that the hole remains perfectly circular. The best solution is to use plaster moulds shaped precisely to support the stopper in its original form. The use of suitable lubricants or starting fluids to facilitate entry into the rubber is also recommended. Even so,

this remains very much a workshop improvisation rather than a true manufacturing process. Note that manually operated professional machines based on the same principle do exist, but they are generally very expensive.

Silicone stoppers are now available from specialist suppliers, both perforated and unperforated. They offer certain advantages over rubber stoppers, and when unperforated, are considerably easier to modify than their rubber counterparts. It is even possible to manufacture them inexpensively and to any desired dimensions. To do so, one may select a commercially available stopper, coat it lightly with petroleum jelly, and place it upright in a plastic or metal box, ensuring a clearance of roughly two centimetres between the stopper and each wall of the box. Plaster is then poured around the stopper without exceeding its height. Once the plaster has hardened, the stopper is removed, leaving behind a perfect mould into which silicone from an ordinary sanitary-grade silicone cartridge can be introduced. Such cartridges are available from virtually every hardware store. If one wishes to provide the stopper with one or more openings, it is sufficient to place one or more glass tubes of appropriate diameter into the mould before the silicone is introduced. These tubes should also be coated lightly with petroleum jelly. This method is particularly valuable for manufacturing stoppers with a central opening whose diameter exceeds half that of the stopper itself, since such items are generally unavailable commercially.

1.2.5 PTFE (Teflon)

In 1945, the American company DuPont de Nemours patented a new material: polytetrafluoroethylene (PTFE), which it marketed under the name Teflon. This material was characterised by its low coefficient of friction and its remarkable chemical inertness.

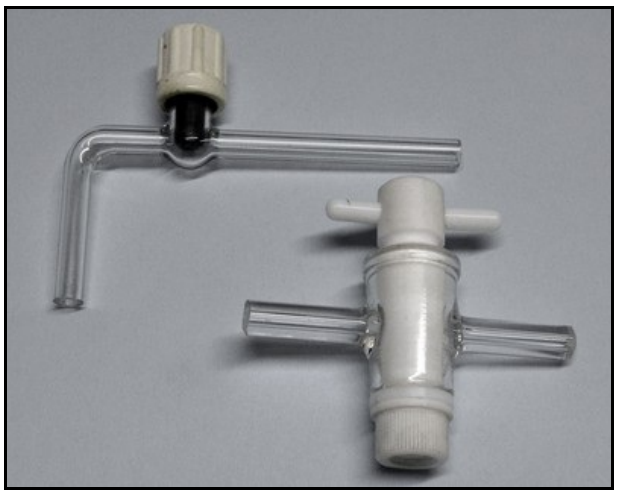


Figure 11

Around 1965, in Belgium, a highly talented glassblower, Mr. Segers, conceived the idea of using a flexible plug coated with a thin layer of Teflon to manufacture an entirely new type of laboratory stopcock operated by precise screw adjustment. He called it the Tefloflex for which he obtained a patent (left-hand side of Figure 11). I had the privilege of knowing Mr. Segers personally. When I was still a very young man, he kindly offered me one of his first Tefloflex stopcocks. Many years later, he spoke to me of his disappointment that the Tefloflex had never achieved the success he believed it deserved. According to Mr. Segers himself, commercial pressures following the

introduction of competing PTFE stopcock designs contributed to the rapid disappearance of his invention from the market, despite its exceptional precision and reliability. Since then, stopcocks fitted with rigid PTFE plugs have become widely established for use on burettes, separatory funnels, and similar apparatus (right-hand side of Figure 11). Their principal advantage is that, unlike glass stopcocks, they require no lubrication. Having used both systems, I still consider the Tefloflex to have been one of the most ingenious laboratory stopcock designs ever developed and one can therefore only regret that such an ingenious invention disappeared from the market.

Following the introduction of these stopcocks, the growing commercial availability of PTFE led to the appearance of new types of laboratory equipment made from this material. Among the best known and most widely used today are beakers and even flasks. Figure 12 shows various items manufactured entirely from PTFE or incorporating PTFE components. Among the latter can be seen, rather unusually, a large condenser whose central tube, fitted with standardised ground-glass joints at both ends, is made entirely of PTFE, while the outer water jacket is made of borosilicate glass 3.3. The two parts are connected by leak-tight silicone seals.

Figure 12

The advantages of PTFE are undeniable, particularly with regard to its resistance to certain chemical substances. Nevertheless, it is far from being a miracle material. Not only does PTFE begin to decompose at temperatures as low as 260°C, but despite its low coefficient of friction, a PTFE plug is not always as easy to manipulate with precision as a well-greased glass plug.

For amateur chemists, I therefore recommend choosing glass stopcocks rather than those fitted with PTFE plugs. As for other PTFE laboratory items, their principal usefulness lies in handling the dangerous substance known as hydrofluoric acid, which will in any case not be discussed anywhere in this book. Hydrofluoric acid has the property of attacking glass, and a single drop on a finger may very well result in amputation. In my opinion, it is one of those substances THAT HAS ABSOLUTELY NO PLACE in an amateur laboratory.

1.2.6 Heating Equipment

Among gas-fired heating devices, the most common are the classic Bunsen burner, designed by the German chemist Robert Bunsen (right-hand side of Figure 13), and the larger Meker burner (Figure 14), invented by the French chemist Georges Meker. The latter, fitted with a wire mesh at the top of the burner tube, is particularly well suited to heating crucibles. Mention should also be made of the Teclu burner, invented by the Romanian chemist Nicolae Teclu. This burner produces a somewhat hotter flame than the Bunsen burner and can readily be recognised by the conical base of its burner tube. All these burners may be supplied either with or without a gas control valve and either with or without a safety pilot flame. Naturally, they must be operated with the type of gas for which they were originally designed, although certain models are described as multi-gas burners. Several burners may also be combined to form heating ramps capable of warming refractory tubes or similar apparatus over lengths of 10 to 20 cm (left-hand side of Figure 13).

Figure 13

Figure 14

In the case of Bunsen and Meker burners, it is often more practical to use bent models, that is, burners which, instead of standing vertically, are arranged horizontally and curved at their outlet end. Figure 14 shows both a straight and a bent Meker burner. Although far less common than traditional models, these burners offer significant space savings in tall assemblies such as certain distillation setups. The bent Meker burner shown in Figure 14 can also be mounted on its

circular base in two different ways, allowing the flame to be directed either horizontally or vertically.

The well-known blue portable Bunsen burner marketed by Camping Gaz operates from a small gas cartridge. Earlier models had the disadvantage of leaving this cartridge exposed, making it vulnerable to attack by corrosive chemicals. In more recent models, the cartridge is better protected, although only on its upper surface. Another manufacturer offers a portable burner whose cartridge is enclosed within a protective plastic shroud (see Figure 15).

Figure 15

A portable gas torch to which various burner heads can be attached—including a broad, flat flame head often called a butterfly burner—can be extremely useful for heating crucibles or bending glass tubing of modest diameter. Such torches are now available at reasonable prices from hardware stores. When purchasing one, it is advisable to select the type of gas cartridge capable of producing the highest attainable temperature consistent with its composition.

The same hardware stores, and even the camping sections of certain supermarkets, often sell highly efficient portable gas stoves at very modest prices. These appliances are fitted with piezoelectric ignition and operate from easily replaceable gas cartridges. When not in use, the cartridge can be disconnected simply by operating a lever that is automatically released when the stove is placed in its protective carrying case, providing a high degree of safety.

The most delicate problem associated with gas heating is that a glass vessel should be heated as uniformly as possible. With the exception of test tubes, a flame should never be applied directly to a glass vessel, even if it is made from borosilicate glass 3.3. Traditional laboratory equipment therefore includes two types of generally square accessories: simple wire gauzes and wire gauzes whose centre is coated with a ceramic layer. The latter distribute heat much more effectively than the former and are particularly useful when slow heating is required. These gauzes are suitable for vessels with flat bottoms, but what should be done in the case of a round-bottom flask? I recommend using fine stainless-steel meshes that can often be recovered from kitchen utensils such as chinois strainers or sieves. These adapt remarkably well to the curved body of a flask. Attention should be drawn to an important point rarely mentioned in chemistry textbooks: the use of wire gauzes, which effectively interrupt the flame, leads to the formation of toxic carbon monoxide. Adequate ventilation should therefore always be provided.

There is another accessory that may be placed between the wall of a borosilicate-glass vessel and the flame of a Bunsen burner. It consists of a square red plate identical to those used on ceramic-glass cooking hobs. Manufactured by Schott in a single size, this plate is available only from specialist suppliers and is normally used together with a dedicated square metal support into which it fits. It allows a

bottle or flask to be heated gradually while distributing evenly the heat supplied by the single burner flame. However, it is suitable only for flat-bottom vessels. A resourceful experimenter may also recover the same type of red plate from a domestic electric cooking hob that is no longer serviceable.

As for electric heating devices, mention must first be made of the traditional circular hotplate concealing an electrical resistance element beneath a metal surface. Such hotplates are suitable for flat-bottom vessels but should be avoided when heating flammable substances whose vapours could ignite or explode upon contact with the very hot surface of the plate.

Professional laboratories are often equipped with electric heating mantles (see Figure 16). These are expensive to purchase, consume considerable amounts of energy, and are generally designed for only one flask diameter, making it necessary to own several mantles if flasks of different sizes are used. Their popularity stems from the fact that they conform closely to the shape of a round-bottom flask, thereby providing exceptionally uniform heating. This is their principal advantage. Some mantles incorporate a circular opening in the centre of their base, theoretically allowing liquids to escape in the event of flask breakage or overflow. Theoretically, I say, because it is obvious that any liquid will first flow over the electrical heating element itself. Like hotplates, heating mantles retain a significant amount of residual heat after the power has been switched off. For this reason, they are poorly suited to reactions liable to run out of control, which explains the usefulness of laboratory jacks already discussed earlier.

Figure 16

For the same reason, some heating mantles are equipped with a particularly useful accessory that allows them to be attached to the vertical rod of a support stand, much as one would attach a clamp by means of a bosshead. The mantle visible on the right-hand side of Figure 20 is of this type. If a reaction begins to accelerate unexpectedly, it is sufficient to loosen the attachment and lower the mantle along

the stand rod, thereby interrupting the transfer of heat immediately.

Many years ago, electric mantles consisting solely of the bare heating element, without any protective housing, were widely used. Less expensive than modern models, they were lightweight and could be positioned by means of a metal ring welded to a rod held in place by a clamp. Despite their practicality and low weight, such mantles have now almost disappeared.

Another type of electric heating device employs a powerful stream of hot air passing through a kind of vertical chimney. Such apparatus is used mainly for heating test tubes uniformly. Yet another type operates by means of an electrical resistance whose thermal radiation is concentrated by a metallic reflector. These devices are expensive to purchase, consume large amounts of energy, and offer only one real advantage: they can deliver a considerable quantity of heat very rapidly. Consequently, they are truly useful only in certain specialised professional laboratories.

At least one amateur chemist on YouTube has demonstrated the use of a heat gun as a laboratory heating device. Although the idea may initially appear ingenious, it is one that SHOULD BE FIRMLY REJECTED because heat guns, like hair dryers, operate by drawing in air from the surrounding room and passing it directly over an electrical heating element brought to red heat. One can easily imagine what might happen if the laboratory atmosphere contains flammable or explosive vapours.

What conclusion should be drawn from all of the foregoing?

Simply that every heating method has its own advantages and disadvantages, and that the best approach is to employ several different systems according to the specific requirements of each experiment.

1.2.7 The Epiradiator

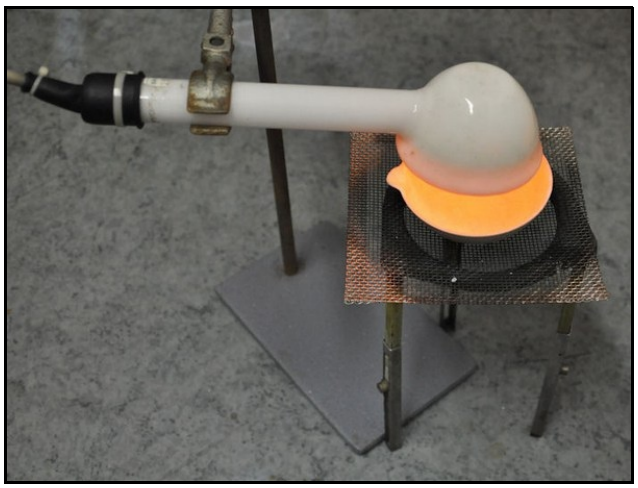


Figure 17

The epiradiator (Figure 17) is a little-known device that can nevertheless render extremely valuable service. Unfortunately, it is extraordinarily expensive, and few school or amateur laboratories are equipped with one. Constructed entirely from silica, it consists of a long handle terminating in a dome-shaped head. Within this dome is housed an infrared heating element. The flat face of the dome is positioned above a solution that is to

be evaporated, after which the apparatus is switched on. No matter how acidic or caustic the solution may be, the liquid evaporates rapidly without risk of damaging the instrument, and the resulting salt is obtained perfectly dry without undergoing the rapid decomposition that often accompanies heating in a dish over a Bunsen burner. Epiradiators are available in various sizes, depending on their electrical power and, consequently, on their ability to act rapidly upon larger or smaller volumes of solution. Because of the intense heat they produce, it is important to keep these devices well away from flammable materials and even from objects liable to deform under heat. For obvious reasons, an epiradiator is entirely unsuitable for the evaporation of solutions containing flammable solvents.

IMPORTANT REMARK

The terms solution and dissolution should not be confused.

A solution is a liquid consisting of a solvent—most often water—in which a substance has been dissolved homogeneously. The process by which this occurs is called dissolution.

1.2.8 Stirrers

Several types of automatic devices are available for stirring liquids and the substances that may be suspended or dissolved within them.

The most common and least expensive are magnetic stirrers. Their operating principle is straightforward: a metallic bar rotates beneath a flat surface upon which the vessel containing the liquid is placed. Inside this vessel is a magnet enclosed within a PTFE-coated bar. When the lower bar begins to rotate, it drives the PTFE-coated magnetic bar, whose motion creates a vortex within the liquid. Figure 18 shows three stirrers of this type. The model on the left is a small unit suitable for modest quantities of liquid. Inexpensive though it is, it is unsuited to large volumes or highly viscous liquids. Furthermore, it is equipped with only a single control knob governing both start-up and rotational speed. At the centre of the illustration can be seen a professional stirrer intended for larger volumes. It is equipped with an on/off switch, a separate speed-control knob, and even a display showing the rotational speed precisely. On the right is a stirrer incorporating a heating plate. Such instruments should be equipped with at least an on/off switch and two additional controls, one for adjusting the stirring speed and the other for regulating the temperature. Only the two larger instruments are fitted with an earth connection. In addition, both possess, at the rear of their horizontal housing, a threaded opening into which a vertical rod may be fixed. They can therefore serve as genuine support stands for lightweight apparatus.

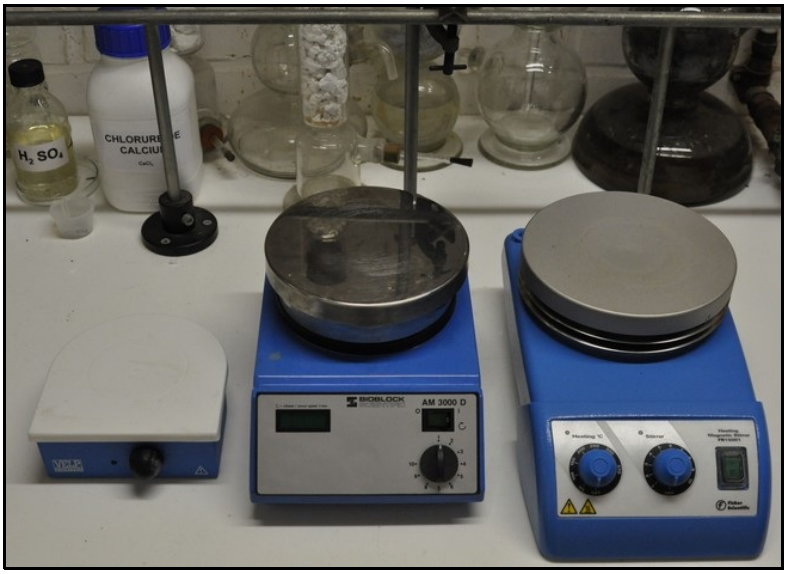


Figure 18

Although highly expensive, heated magnetic stirrers consume considerable amounts of energy and are surprisingly inefficient as heating devices. Much of the heat generated by the plate is simply dissipated into the surroundings, while the plate itself does not heat uniformly. As a result, it takes a long time to raise even a moderate volume of liquid to the desired temperature. I therefore do not particularly recommend the purchase of such instruments for beginners. I would also advise avoiding certain inexpensive Chinese devices that claim to combine stirring and heating functions while being equipped with a heating plate of very limited diameter. Not only are they fragile and inefficient, but they may even topple over if an object weighing only a few hundred grams is attached to the vertical rod positioned well outside the centre of gravity of the instrument.

Paddle or shaft stirrers constitute another category of equipment. They are less frequently used than magnetic stirrers and are considerably more expensive. They generally consist of a motor positioned above the vessel containing the liquid to be stirred. This motor is fitted with a chuck similar to that of a drill, into which may be secured either a stainless-steel shaft or a glass shaft extending directly into the liquid. The shape of the shaft tip, together with the adjustable rotational speed, makes it possible to generate a more or less powerful vortex capable of stirring the liquid vigorously. Such stirrers become indispensable when dealing with very large volumes or highly viscous liquids. Most of these motors are both powerful and heavy. They should therefore preferably be mounted on a rigid framework firmly attached to the laboratory bench or on a special stand provided with a very broad base.

Several types of stirrer belonging to this category are available. Figure 19 shows three examples. In the centre is a relatively small model formerly marketed by Prolabo (France). On the left is a substantially larger instrument manufactured by the prestigious German company IKA. Both are electromechanical devices. The IKA model provides two speed ranges that must be selected manually while the

instrument is stopped. On the right, however, can be seen another IKA instrument that is entirely electronic. It offers continuously variable speed control simply by turning a single knob on the front panel. The rotational speed is also displayed digitally. In every case, the stirring shaft held in the chuck can pass completely through the body of the instrument, making it possible to stir successively the contents of vessels of different sizes without altering the position of the motor itself. One merely loosens the chuck and raises or lowers the shaft as required. In this respect, and in their ability to operate for long periods without overheating, these instruments differ significantly from ordinary drills, even though the basic principle is similar.

Figure 19

Taking these fundamental differences into account, a skilled hobbyist can nevertheless construct such a stirrer from a drill equipped with a good speed regulator. The stirring shaft itself may be made from a solid glass rod whose lower end is suitably bent, or from a straight solid glass rod to which three trimmed cable ties are attached so as to form three blades arranged in a triangular pattern. The builder should remember, however, that such a homemade device will operate satisfactorily only for relatively short periods. Furthermore, each time a different vessel is used, the drill itself will have to be raised or lowered on its support, assuming that an adequate mounting system has been provided.

Depending on the application, the vessel containing the liquid may either remain open or be fitted with a special PTFE or glass sealing system. The PTFE version consists simply of a ground PTFE stopper pierced centrally, the PTFE itself being expected to provide the seal around the vertically moving shaft. The glass version is more elaborate and may be compared to a sort of triple bell arrangement in which the sealing system is immersed in mercury.

Figure 24

There exists another type of shaft stirrer that is rarely used despite its extraordinary efficiency. In this device, agitation is produced by a shaft carrying at its lower end a metal or glass disc perforated with numerous holes. Through the action of electromagnets, the shaft and disc are subjected to a small-amplitude but high-frequency vertical oscillation. This motion produces such vigorous mixing that it can rapidly emulsify two immiscible liquids, such as water and oil. Another advantage is that the operating principle generates virtually no wear and very little heating of the components. Figure 24 shows one of these stirrers, a Vibromix, in operation. The agitation is so vigorous that a veritable column of liquid forms around the stirring

shaft, while foam appears around the inner wall of the vessel.

Because of the diameter of the stirring discs, this apparatus must be used with a wide-neck vessel. The longer the neck, the lower the risk of splashing outside the container. Originally, the instrument was supplied with an accessory intended to permit operation in a hermetically sealed vessel. My own experiments suggest that this possibility was somewhat overstated. The high-frequency vibration of the shaft is not particularly compatible with any truly airtight sealing system, at least not in the case of this instrument. Other devices based on the same principle exist, but they are generally much larger and intended exclusively for industrial use.

Besides its remarkable stirring efficiency, the Vibromix offers another advantage. Its ordinary stirring shaft can be replaced by a hollow shaft that may be connected to a source of gas intended either to dissolve in the liquid or to react with it. I have never personally needed to test this possibility, but I believe it deserved to be mentioned.

Figure 25

Another type of stirrer frequently encountered in laboratories, but one that an amateur can easily do without, is the vortex mixer. In its most common form (Figure 25), the upper part of the instrument carries a cup-shaped plastic support capable of accommodating the bottom of a test tube up to approximately 30 mm in diameter. This support is driven by an orbital motion which produces within the liquid an extremely powerful vortex capable of dissolving solid substances very rapidly. The instrument may operate continuously or only when a test tube is pressed against the upper support. The speed of the orbital motion—and therefore the intensity of the vortex—is adjustable, and an on/off switch is provided. The best instruments of this type, such as the IKA model shown in the illustration, include recessed side grips that facilitate carrying them around the laboratory bench.

The imagination of chemists and manufacturers being virtually limitless, many other types of mechanical and electronic stirrers exist. Some relatively uncommon models operate by means of pulleys or compressed air. Others are fitted with clamps capable of various motions and designed to hold different types of vessels. Still others employ large platforms moving in a horizontal orbital motion around a central point or in a vertical motion resembling that of a swing. The speed of these movements may range from very slow to relatively rapid. The vessels—often flat containers such as culture flasks—are secured to the platform by various means using the slots provided around its perimeter. These instruments are generally equipped with timers and are intended primarily for microbiological work, although they are also useful in certain chemical applications.

1.2.9 Distillation and Cooling

Many people today wish to undertake distillation operations in order to obtain alcoholic beverages or natural essences. What they generally fail to realise is that laboratory apparatus is entirely unsuited to such purposes, since it was never designed to handle the large quantities of material required for even modest production. Those interested in such activities should therefore turn to metal equipment, usually made of copper.

Perhaps under the influence of certain statements found on the Internet, the Vigreux column has become something of a favourite accessory among amateur distillers. In reality, matters are rather different, and I shall explain why later.

The principal component of laboratory distillation equipment is the condenser, which is usually made of borosilicate glass 3.3. Several types are available. The simplest is the straight condenser, consisting merely of a straight inner tube enclosed within an outer jacket through which cold water circulates. The Allihn condenser, sometimes called a bulb condenser, differs from the straight condenser in that its inner tube is formed by a series of bulbous enlargements designed to increase heat exchange. Both of these condensers may be used in positions ranging from a slight inclination to complete verticality. A third type is the coil condenser. Here, the central tube takes the form of a coil, thereby increasing both the surface area and the contact time between the cold water and the hot vapours passing through it. In order to ensure proper drainage of condensed liquids, coil condensers must always be operated in a vertical position. Finally, there is the Dimroth condenser, named after the German chemist Otto Dimroth. In this design, the arrangement is reversed: cold water circulates through the central coil while the vapours pass through the outer tube surrounding it. Some Dimroth condensers even employ a double-water-circulation system in which two coils are intimately intertwined.

Many modern condensers are fitted at both ends with standardised ground-glass joints—one male and the other female—which permit a wide variety of assemblies through the successive connection of adapters and vessels, whether single-necked or multi-necked. This arrangement is convenient and eliminates the need for rubber or silicone stoppers that might be attacked by certain chemicals.

Nevertheless, because of the cost of ground-glass apparatus, many chemists still employ condensers without standard joints, connecting them instead to various types of flasks by means of suitable stoppers. The simplest vessel for this purpose is the distillation flask. Unlike an ordinary flask, it possesses a side arm through which vapours may be directed towards the condenser. This side arm is usually inclined downward so that it can readily be connected to an inclined condenser, although it may also be curved vertically downward for connection to a coil condenser.

Certain distillations require liquid to be added gradually to the flask, either to intensify a reaction or simply to introduce additional material for distillation. Since the main neck of a simple distillation flask is normally closed by a stopper carrying a thermometer, the German chemist Ludwig Claisen devised a different type of flask fitted with a second neck attached laterally to the principal one.

In the Claisen flask, the principal neck could therefore be used for the gradual addition of liquid.

In both ordinary distillation flasks and Claisen flasks, the thermometer bulb should always be positioned near the entrance to the side arm so that it accurately measures the temperature of the vapours entering the condenser.

Today, Claisen flasks have virtually disappeared from laboratories, having been replaced by multi-neck flasks fitted with standardised ground-glass joints. The most common arrangement employs a three-neck flask, whose necks may be either vertical or inclined. One neck is connected to a dropping funnel, another accommodates a thermometer measuring vapour temperature, and the third communicates with the condenser through an adapter. These relatively expensive two- and three-neck flasks may themselves be replaced by an ordinary flask fitted with a ground joint that accepts a two- or three-arm adapter according to the needs of the experiment (Figure 26).

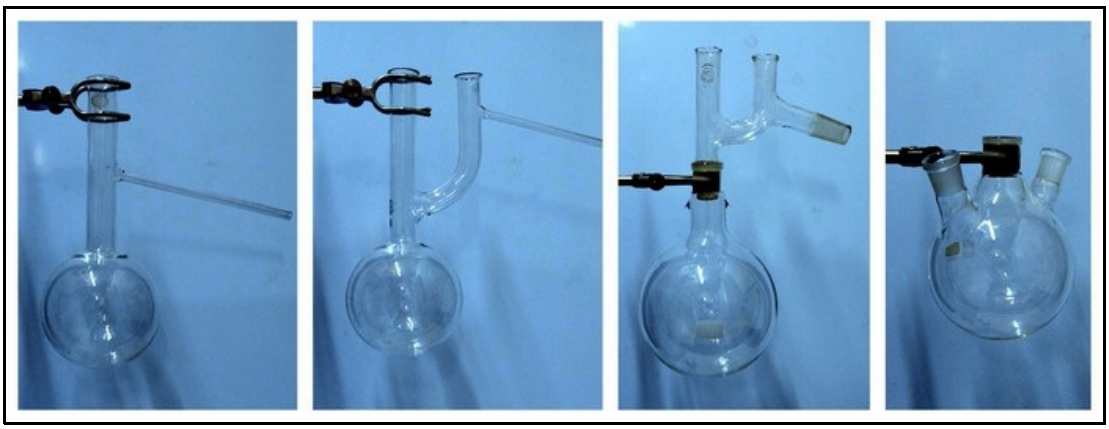


Figure 26
From left to right: an ordinary distillation flask with side arm, a Claisen flask, a flask fitted with a double ground-glass adapter, and a three-neck flask.

The thermometer mentioned above passes either through a rubber stopper in simple assemblies or through a special fitting in assemblies constructed entirely from ground-glass apparatus. Figure 27 shows two different types of such fittings. From left to right can be seen a male ground joint fitted with the actual thermometer adapter, consisting of a flexible PTFE-coated sealing ring tightened around the thermometer by means of a screw cap. To its right is the same device mounted on an adapter. Further to the right is a male ground joint consisting of a sealed tube that can be filled with liquid and into which the thermometer is inserted. The

temperature of the liquid is transmitted to the thermometer. At the far right is the same type of sealed tube mounted in a bent adapter.

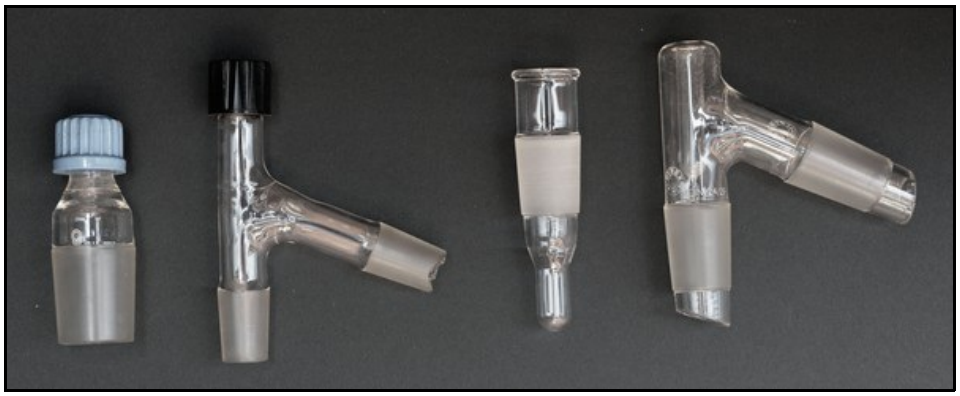


Figure 27

Each of these two major systems presents disadvantages. Adapters employing flexible sealing rings often suffer from imperfect sealing, as is frequently the case whenever such rings are used. The alternative design, on the other hand, introduces a liquid bath that slightly delays the transmission of the true temperature to the thermometer. Nothing is perfect, even in chemistry!

At the outlet of the condenser, a curved adapter may be attached in order to direct the distillate vertically into any convenient receiver open to the atmosphere. Alternatively, a more sophisticated ground-glass adapter may be employed. Such adapters incorporate a side arm allowing either the evacuation of gases or operation under reduced pressure, the latter being intended to lower the boiling point of the liquid being distilled.

The apparatus described so far applies only to simple distillation and condensation. We must now turn to fractional distillation.

Its purpose is to separate substances whose boiling points differ sufficiently from one another. For this purpose, a Vigreux column may be employed. This consists of a vertical glass tube placed above the body of the distillation flask and provided internally with a series of downward-pointing glass projections arranged at intervals. These projections serve to condense the less volatile vapours while allowing the more volatile ones to continue rising through the column and therefore to distil first. The temperature recorded by the thermometer positioned near the outlet leading to the condenser remains constant for a time, then rises, stabilises again, and so forth. In this way, two, three, or even four substances possessing different boiling points may be separated and collected successively in different receiving vessels.

Older Vigreux columns were constricted at their lower end so as to form a narrow tube capable of passing through a stopper. This tube was so narrow that condensed liquid returned to the flask only with difficulty because it was opposed by the

ascending vapours. Such columns, now encountered only on the second-hand market, should be avoided. Modern Vigreux columns fitted with a sufficiently wide lower ground joint should be preferred, since they permit the simultaneous circulation of ascending vapours and descending condensate.

The Vigreux column may advantageously be replaced by a vertical tube filled with Raschig rings, named after the German chemist Friedrich August Raschig who invented the concept. These rings perform the same function as the projections of a Vigreux column but generally with greater efficiency because the surface area available for vapour contact is considerably larger. Raschig rings, retained for example by a perforated PVC or PTFE disc at the base of the column, may be made of glass or ceramic and may even be replaced by glass beads. Some columns of this type are enclosed within a second tube, the air space between the two acting as thermal insulation from external influences.

A third type of column exists, although it is rarely employed by amateur chemists. It consists of a glass tube containing, at intervals, plugs of metallic wool similar to scouring pads. Here again, the objective is to maximise contact between ascending vapours and surfaces capable of condensing them.

Everything discussed so far relates, strictly speaking, only to distillation. In the laboratory, however, it is sometimes necessary to cool substances other than hot vapours, and in such cases systems quite different from the condensers described above are employed.

In certain cases, it is gases that must be cooled very intensively, either to liquefy them or to dry them. Professional laboratories frequently use liquid nitrogen for this purpose, its temperature approaching –200°C. The use of liquid nitrogen, however, requires equipment and infrastructure that amateur laboratories cannot realistically possess. Amateur chemists therefore rely instead on cooling mixtures, that is to say, substances which, when mixed together, produce a greater or lesser degree of cold. Many such mixtures exist. The three most commonly used are the water–ice mixture, which stabilises at 0°C; crushed ice mixed with fine table salt, which allows temperatures several degrees below zero to be reached; and crushed ice mixed with calcium chloride (non-anhydrous), which permits temperatures below –40°C to be obtained. Several examples of such mixtures are given in Addendum No. 5, although many others exist.These cooling mixtures may be placed either in a flexible container such as a PVC bag or in a large vessel (tank or beaker) surrounding the flask or tube that is to be cooled. Figure 28 shows a more sophisticated device inspired by certain older arrangements: a glass vessel intended to contain the cooling mixture and through which passes a glass coil. This apparatus, which

Figure 28

was the last item personally blown by Mr. Segers, founder of the companies MSL and Sadems, mentioned earlier, is fitted at its lower end with a ground-glass joint designed to connect directly to the neck of a receiving flask. Such a device is suitable not only for cooling liquids but also for liquefying certain gases as SO_2 for examples. It can accommodate not only conventional cooling mixtures but also dry ice and even liquid nitrogen. This accessory may be insulated from ambient temperature by means of a sleeve made from a flexible sheet of expanded polystyrene lined with aluminium foil.

Inspired by conventional water-cooled condensers, there also exist double-walled glass vessels that may serve quite different purposes based on heat exchange. Figure 29 shows, on the right, a kind of two-neck Woulff bottle fitted with ground-glass joints (one upper and one lower) enclosed within a larger vessel. Through two small side tubes, a hot or cold liquid may be circulated in the space between the walls, thereby heating or cooling whatever is contained in—or passes through—the inner two-neck vessel. The same illustration shows, on the left, an open beaker surrounded by a double wall that may be used in two different ways. Either a very cold solid mixture or a very hot liquid may be placed in the beaker itself, causing the liquid or gas circulating through the double wall to be cooled or heated accordingly; or a hot or cold liquid may be circulated through the double wall in order to cool or maintain at temperature a liquid contained in the open beaker.

Figure 29

Other types of glassware also exist for cooling, heating, or maintaining gases and liquids at constant temperature. Among them, special mention must be made of Dewar vessels, which are essentially improved vacuum flasks generally provided with a relatively wide opening. These vessels are commonly used for experiments involving liquid nitrogen and even for its transport. Such equipment, inspired by the familiar vacuum flask, has rather limited usefulness in an amateur laboratory.

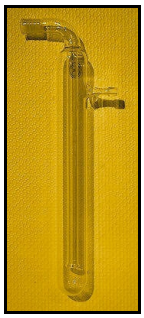


Figure 30

Before leaving the subject of refrigeration, a few words should be said about another type of apparatus known as a cold trap (Figure 30). It consists of a thin-walled glass tube into whose centre extends a second tube through which a gas enters before leaving through a side outlet at the top. The entire apparatus is immersed in a cold bath of carefully selected composition. The moisture contained in the gas is thus trapped in the form of crystals without liquefying the gas itself. This type of apparatus is generally manufactured as a permanently sealed unit since, in principle, it does not require internal cleaning.

1.2.10 Filtration

In a chemistry laboratory, filtration is a frequent operation, and there now exists a multitude of specialised devices and accessories for carrying it out. It is worth saying a few words about the most useful and least expensive among them.

The simplest filtration system is the one that uses filter paper placed in a conical funnel. In the specialised trade, two types of filter paper are available: those supplied as circular discs and those which, when unfolded, open into a pleated cone. The latter are ready for immediate use, whereas the former must be folded into quarters before being inserted into the funnel, whose walls they then line in a flat manner. Because pleated filters offer a greater surface area than flat filters, they provide faster filtration. Naturally, these filters are available in a wide range of sizes suited to different funnel diameters, and in a considerable variety of porosities adapted to the particle size of the substances to be retained. Some filter papers are even designed to be incinerated while leaving almost no ash, an important consideration in professional laboratories where highly precise weighings are required.

Figure 31

Traditional glass funnels are generally conical in shape, smooth both inside and outside, and fitted with an outlet stem whose length varies according to the model. They are available both in soda-lime glass and in borosilicate glass. Certain more sophisticated funnels are provided, on the inside of their conical section, with spiral ribs or longitudinal flutes that improve filtration speed because a non-pleated filter paper can no longer adhere directly to the entire inner surface of the funnel. Figure 31 shows, on the left, a conventional funnel and, in the centre and on the right, funnels provided with various types of internal fluting.

A particular type of funnel is the Büchner funnel, named after its inventor, Ernst Büchner. Traditionally made of porcelain, Büchner funnels are now also manufactured from plastic and even from combinations of glass and plastic. One major advantage of plastic Büchner funnels is that they can be unscrewed into two separate parts, making them easier to clean when necessary.

A Büchner funnel consists of a cylindrical upper section whose base is formed by a horizontal perforated plate. This is continued by a conical collecting section terminating in a tube designed to fit into a special conical stopper. The principle of operation is simple: a circular filter paper is placed upon the perforated plate, and the liquid-solid mixture is poured slowly onto the centre of the paper. The solid particles are retained by the filter paper while the liquid passes through the perforations.

The Büchner funnel is generally mounted on a filtering Erlenmeyer flask by means of a conical stopper specially shaped to match the outlet tube, thereby ensuring a good seal between the two pieces of apparatus. This type of Erlenmeyer flask is distinguished by the presence of a side arm to which a tube connected to a vacuum pump may be attached. By creating a vacuum within the flask, filtration is accelerated while ensuring that the filter-paper disc remains firmly pressed against the perforated plate of the Büchner funnel.

Figure 32

Many filtering Erlenmeyer flasks are made from very thick borosilicate glass. They should therefore not be heated in the same manner as ordinary Erlenmeyer flasks, since doing so may cause them to crack or even shatter. Instead of filtering Erlenmeyer flasks, some manufacturers offer cylindrical bottles likewise fitted with a side arm for vacuum applications. Figure 32 shows a large Büchner funnel 21 cm in diameter mounted on a 2-litre filtering Erlenmeyer flask, together with a more conventional 11 cm Büchner funnel (whose perforated plate is clearly visible) and a series of special rubber conical stoppers perfectly adapted to the outlet tubes of Büchner funnels of different sizes.

Finally, there is another category of filters that deserves mention: those incorporating a porous sintered-glass disc permanently fused into the funnel itself and through which filtration takes place. Most of these filters have a cylindrical-conical shape, although some are of the more traditional conical form.

The sintered-glass discs are available in several grades of porosity, selected according to the fineness of the solid substances to be collected.

The principal advantage of these filters is their great durability and their ability to be used with substances that would attack ordinary filter paper. Their disadvantage is that cleaning the sintered-glass disc after use is not always easy. One must employ a reagent capable of vigorously attacking the solid material that has become lodged within the pores of the filter. These funnels are always used in conjunction with a vacuum pump and, consequently, generally with a filtering Erlenmeyer flask. Indeed, they would not function satisfactorily under the influence of gravity alone.

1.2.11 Drying

It is often necessary to dry a precipitate collected by filtration or decantation, or even a solution containing a salt that one wishes to recover in crystalline form. Of course, a simple method is to proceed in full sunlight during summer or on a radiator during winter. There are cases, however, where such improvised methods are unsuitable because the salt to be recovered attracts moisture from the air and partially dissolves in it. In such circumstances, a desiccator must be used (Figure 33).

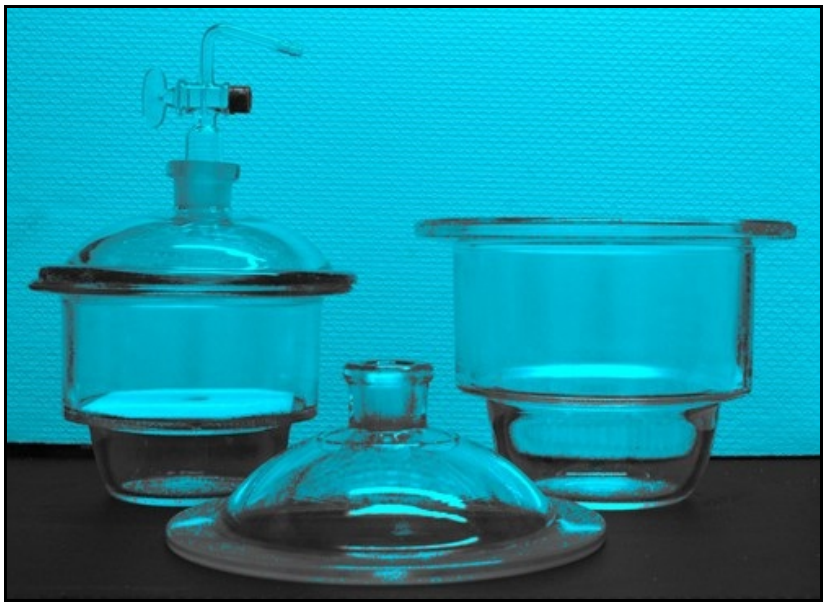


Figure 33

A desiccator is a kind of large vessel somewhat resembling a confectionery jar and consisting of three parts. The principal component is the vessel itself, whose lower section is narrower than its upper part. This vessel is closed by a removable lid that fits hermetically onto a broad rim by means of a grease similar to that used for glass stopcocks. This lid often incorporates a ground-glass socket into which fits a greased stopcock through which the apparatus may be connected to a vacuum pump.

Alternatively, although less commonly, this connection may be located on the body of the desiccator itself. Finally, resting within the lower part of the vessel, there is a perforated platform, usually made of porcelain and sometimes of plastic.

The operating principle of the desiccator is straightforward. The substance to be dried, placed in a crystallising dish, is set upon the perforated platform, while the bottom compartment is filled with a substance capable of absorbing moisture, such as concentrated sulphuric acid. The vacuum is not truly essential, but it accelerates the drying process.

Desiccators were formerly manufactured from ordinary laboratory glass. Later they were produced in borosilicate glass 3.3, which was not really a useful improvement. Some were even made from actinic-resistant glass. Today, plastic desiccators are available. Their advantages are that they are less expensive, less fragile, and lighter than their glass counterparts. Naturally, these instruments are manufactured in a variety of sizes.

Note: A desiccator may also be used for the storage of certain substances, such as solid iron(II) sulphate, which rapidly turns yellow when exposed to air.

1.2.12 High-Temperature Heating of Solids

There exist many different types of tubes and crucibles (with or without lids) intended for heating solid substances to high temperatures. The most common are made of porcelain and are relatively fragile. Others, more expensive but more resistant and capable of withstanding higher temperatures, are manufactured from alumina or other refractory materials. Such equipment can generally be purchased only from specialist suppliers or obtained second-hand. In some cases, unfortunately, these items can be used only once because effective cleaning proves impossible.

Another heating accessory frequently mentioned in chemistry books is the bulb tube, made of low-expansion glass or borosilicate glass 3.3. These tubes are fragile simply because they are often subjected to severe thermal stresses concentrated over a small area, generating tensions that may cause the glass to shatter during cooling. Rather than using costly bulb tubes, I therefore recommend employing cylindrical borosilicate-glass 3.3 tubes, which a glassblower can usually supply at modest cost. If one of them is sacrificed during an experiment, it will be with considerably less regret.

Silica tubes are another alternative worth considering, although they are significantly more expensive. Because their coefficient of expansion is almost zero, they are even more resistant to temperature variations than borosilicate glass 3.3. Nevertheless, it should be remembered that, in rare cases, even silica tubes may break.

Warning: All of these materials may sometimes react with certain substances and, as a consequence, become permanently stained or even develop holes.

1.2.13 Chemicals

In older chemistry books, it is common to find passages in which the taste of chemical substances is described in more or less detail. Tasting chemicals is, however, one of the most dangerous things anyone can do, since some substances are capable of attacking the mucous membranes of the mouth and tongue directly, while others are highly poisonous. This old practice, which has fortunately disappeared, belongs to a time when chemists had very few instruments or machines capable of helping them identify a substance quickly. As a first step, they therefore relied on their five senses: sight (shape, color...), touch (rough, silky...), hearing (effervescence, crackling sounds), smell and, inevitably... taste. Only afterward did they perform chemical analyses in test tubes. Fortunately, the human sense of taste is so sensitive that only extremely small quantities of a substance were needed to provide a fairly good idea of what it might be.

Over the years, the toxicity of a great many substances gradually became apparent. Chemicals may affect living organisms in several different ways: through simple contact with the skin, by being inhaled as gases, vapors, or fine particles, or by being swallowed accidentally. Every chemist, especially beginners and amateur experimenters, should always bear in mind that the the vast majority of chemicals are harmdul or poisonous, depending on the dose. That is why certain basic safety precautions are indispensable.

Regular ventilation of any room where chemicals are used or stored is essential. Chemicals should be kept in suitable bottles rather than in simple cardboard boxes, plastic bags, or metal containers. They should be handled carefully, cautiously, and precisely, making sure they cannot spread uncontrollably onto the laboratory bench, clothing, skin, and especially the eyes. In some cases, in addition to careful and precise handling, wearing gloves or a protective mask may be useful or even essential.

Some chemicals may also prove dangerous because, if handled improperly or mixed with other substances, they may cause fires or explosions.

It would be tedious to list here examples of substances that are dangerous either by themselves or when mixed with others. The best thing any chemist can do is to obtain information online about the specific properties of every chemical purchased and to state clearly on the bottle label the hazards to which anyone handling it may be exposed. This can be done by using the appropriate hazard pictograms, but even better by placing a second, brightly colored label opposite the first. The first label simply identifies the chemical, whereas the second provides a detailed written description of its hazards, including any dangerous reactions that may occur if it is

mixed with other substances.

It is because of their various hazards and their potential misuse for harmful purposes that increasingly strict regulations governing many chemicals have been introduced in countries throughout the world. As a result, their sale has been restricted or prohibited for individuals who do not possess the required qualifications or legal authority to use them. Of course, this directly affects amateur chemists who do not work in officially recognized laboratories. Obtaining certain chemicals therefore becomes increasingly difficult for them. However, with patience and a little ingenuity, some of these restrictions can be worked around.

For the same safety reasons, certain chemicals are, in principle, no longer permitted in schools attended by teenagers. As a result, some experiments can no longer be carried out there. By progressively reducing the range of experiments available to them, many teachers have eventually diminished the experimental aspect of chemistry to such an extent that, today, many young people perceive it as a purely theoretical science.

But, between the recklessness of the past and the paralysis of the present, there remains a middle path: informed experimentation guided by knowledge, observation, and common sense.

1.2.14 Storage Bottles

In earlier times, chemists frequently stored their reagents in all-glass bottles and jars fitted with ground-glass stoppers. Because these stoppers were not standardised, they could not be interchanged from one bottle to another. Moreover, they rarely provided a truly airtight seal, even when new. Such bottles are still commonly encountered at flea markets and antique fairs. While they may be attractive from a historical or decorative standpoint, they are neither practical nor particularly safe in a serious laboratory and must therefore be avoided.

These old bottles suffered from another disadvantage. When they contained solutions of dissolved salts, a small amount of liquid could remain between the stopper and the neck after use. As this liquid slowly evaporated, crystals formed and effectively cemented the stopper in place. Countless chemists have broken bottles—or injured themselves—while attempting to free a stopper trapped in this manner. Modern laboratories have therefore abandoned such containers almost entirely.

Today, they have largely been replaced by thick-walled glass bottles, usually amber in colour, fitted with wide plastic screw caps containing a PTFE liner to improve sealing. The necks of these bottles are often equipped with a plastic anti-drip ring whose flared profile helps prevent liquid from running down the outside of the bottle during pouring. More recent designs dispense with this separate plastic ring

altogether by incorporating a flared anti-drip profile directly into the glass neck itself (Figure 34). From a sealing standpoint, a PTFE liner generally performs better when pressed against a perfectly smooth glass surface than against a plastic ring that may exhibit slight irregularities. Unfortunately, these modern flared necks are not always the easiest to use without spilling a few drops of liquid.

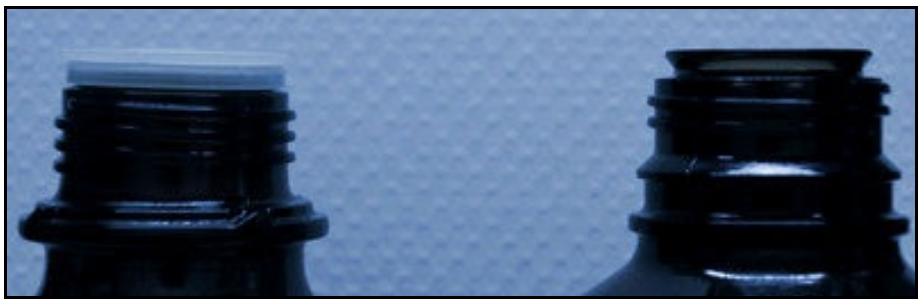


Figure 34

Another type of bottle now widely used in laboratories is commonly referred to as an ISO bottle, although this designation is not entirely accurate. Such bottles are generally fitted with a wide plastic screw cap and an anti-drip ring, although some models replace the latter with a flared glass neck. They are usually manufactured from thick, colourless borosilicate glass, though less expensive soda-lime versions are also available. Certain premium models have an internal actinic-resistant coating of amber colour.

These bottles can be fitted with various types of cap. The most common versions, which cannot even withstand the temperatures of a laboratory steriliser, provide only moderate sealing performance. Others, considerably more expensive and often distinguished by a red cap, incorporate a PTFE-faced sealing disc intended to provide a perfectly airtight closure. In practice, however, the result often falls short of expectations. Despite this, ISO bottles have become extremely popular and have largely replaced the older Sovirel SVL bottles mentioned earlier. Fashion and effective marketing have undoubtedly contributed to their success, and ISO bottles are now available in countless forms: cylindrical, square, recessed for easier handling, and even adapted for use as miniature reactors through the addition of specialised caps carrying various fittings. Their principal drawback is that they cannot be heated as conveniently as flasks, Erlenmeyer flasks, or even ordinary beakers. Furthermore, the considerable thickness of their glass makes the modifications that an experienced glassblower might normally perform far more difficult.

Instead of investing in these relatively costly laboratory bottles, the amateur chemist may prefer ordinary clear or amber glass bottles of the type sold by pharmacies. These bottles typically accept the same style of white plastic screw cap over a range of capacities from 100 mL to 1 litre (Figure 35). The caps provide a reasonably good seal. Care should nevertheless be taken not to overtighten them, as the upper portion of the cap may crack hours or even days later. Such failures can present a

genuine hazard, especially when solvents are involved.

Figure 35

These pharmacy bottles may also be fitted with black plastic caps. Although shorter than the white versions, they are considerably stronger and can easily be used in combination with PVC anti-drip inserts fitted directly into the bottle neck. Together, the cap and anti-drip insert provide both excellent mechanical strength and a reliable seal. Other closures are also available,including soft-plastic or silicone septa held in place by metal caps featuring a central opening. Such bottles allow liquids to be withdrawn conveniently by syringe.

As already mentioned, all of these glass bottles may be either colourless or amber. According to a long-established convention—one that originated primarily in pharmacy, although it is now observed less rigorously than in the past—liquids regarded as hazardous are generally stored in amber bottles. These bottles were originally designed to filter out certain wavelengths of light capable of affecting the substances they contained. Similar considerations once led to the use of blue and green bottles, but these have virtually disappeared from modern laboratories.

1.2.15 Some Special Storage Methods

The storage of both common and less common chemicals requires certain precautions. Some solids and liquids must be protected from sunlight or ultraviolet radiation. It was for this purpose that amber glass bottles were originally developed, followed later by the more costly actinic-resistant glassware whose coloured surface coating was discussed earlier. Even so, it is often wise to store such containers in

cabinets where they remain in complete darkness.

Various well-sealed containers, including those made of PVC, are suitable for storing concentrated sulfuric acid. However, because this acid has such a strong affinity for water, even the smallest trace of acid remaining in the threads of the cap attracts atmospheric moisture. The resulting acid-water mixture may then run from the neck when the bottle is opened, contaminating the workbench or burning the chemist's fingers. If one instinctively wipes the neck or threads with absorbent paper or a cloth, the material may become carbonised and subsequently contaminate the acid itself. For this reason, the only bottle that I consider truly suitable for concentrated sulfuric acid is an old-style bottle made of either amber or clear glass (Figure 36). The neck of this bottle flares outward in the shape of a flower corolla, while its bell-shaped stopper has a ground inner surface that bears against the equally ground outer surface of the corolla. At the center is a removable hollow cylindrical glass insert that fits into the neck by means of a ground-glass joint. This insert is provided with a pouring spout at its upper end and a deep notch at the point where it fits into the neck of the bottle. The operating principle of this type of bottle is as follows. When the bell-shaped stopper is removed, the acid pours more easily through the spout because air can enter the bottle through the notch mentioned above. Once the bottle is returned to the upright position, any acid remaining in the corolla can flow back into the bottle through this same notch. To ensure a perfect seal, the ground surface of the corolla should be lightly greased, and the ground joint of the central insert should be wrapped with sanitary PTFE tape. Paradoxically, although some manufacturers continue to develop new types of laboratory accessories, this type of bottle has disappeared from modern laboratory equipment and can now be found only in antique shops or at flea markets. Do not confuse this bottle with the old or modern "acid bottles" (Figures 37-A and 37-B), which have no removable central insert and instead are simply fitted with a double ground-glass safety closure. Such bottles are also available in a slightly different version in which the "cover" is made of plastic.

Figure 36

Figure 37-A

Figure 37-B

Highly alkaline liquids (including limewater and baryta water) must always be stored in high-density polyethylene (HDPE) bottles because, even at room temperature, they slowly attack glass, causing it to become cloudy. Wide-neck HDPE bottles are also particularly well suited for storing many solid chemicals. It should nevertheless be borne in mind that plastic bottles may deteriorate with age, becoming brittle and developing fine cracks. They should therefore be inspected periodically and replaced as soon as slight crackling sounds can be heard when they are gently squeezed by hand.

The storage of bromine is sometimes considered so delicate that some laboratories prefer to prepare it only as needed. Nevertheless, bromine can be stored with relatively little risk in amber glass bottles fitted with PVC caps provided with a PTFE seal, provided that they are kept in a very cool, well-ventilated place. Over time, bromine attacks the plastic material of the caps. They must therefore be replaced periodically.

The long-term storage of certain highly volatile organic liquids, bromine, or salts dissolved in hydrochloric acid requires perfectly airtight containers. For this purpose, nothing has ever surpassed flame-sealed glass ampoules, which closely resemble—although on a larger scale—the ampoules used for certain pharmaceutical products. Amateur chemists can make such flame-sealed ampoules themselves from the appropriate materials available from specialized laboratory suppliers..

The storage of iodine also presents difficulties because it gradually sublimes regardless of the precautions taken. I recommend storing it in a narrow-neck glass bottle fitted with a cap incorporating a PTFE seal. For even better thermal insulation, this bottle may be placed inside a tightly closing PVC container or, better still, inside a glass preserving jar fitted with a silicone gasket. It should be noted, however, that this outer container will gradually become stained brown as a result of the inevitable sublimation of iodine. Needless to say, iodine and any bottles containing it must be kept in a very cool place and well away from other substances or materials with which it might react.

White phosphorus, supplied in stick form, reacts on contact with air. For this reason, it is stored under previously boiled water, which can easily be removed with a simple piece of filter paper when the phosphorus is needed. The bottle, preferably made of amber glass or, alternatively, black HDPE, should be kept in the dark. The sticks should be cut under water using a plastic or ceramic blade. White phosphorus is now commonly supplied under a layer of oil. In my opinion, this is not the best method of storage because, when the phosphorus is to be used, the oil is more difficult to remove than water.

Sodium reacts with both water and air. Its pieces are now often supplied under oil. However, they are better stored under kerosene, which can be removed much more easily with filter paper before use. The storage bottle should preferably be made of

amber glass. Pieces of this soft metal should be cut with a plastic or ceramic knife on a solid glass or ceramic plate. Metal knives and needles should not be used. Any unused sodium should be returned immediately to its original container, and the freshly cut piece should be used promptly while its surface is still bright.

Potassium has the same characteristics as sodium but is even more reactive. With time, its surface becomes covered with a layer of peroxides that may react explosively with the metal itself or with the solvent used for its storage. Although this metal can still be obtained relatively easily through the Internet, I strongly advise against purchasing it, and especially against storing it. One of my friends nevertheless decided to obtain some and later discovered that the entire surface of the metal had become covered with small crystals. Fortunately, he remembered my warning and cautiously disposed of the entire contents of the bottle.

Hydrogen peroxide may release oxygen upon contact with the slightest trace of organic matter or fine powders, including ordinary dust. It should therefore be stored in narrow-neck high-density polyethylene (HDPE) bottles fitted, whenever possible, with a plastic filter insert serving as a dust trap. The cap itself should be equipped with a special pressure-relief valve. Beware of the plastic containers in which hydrogen peroxide is sold in some home-improvement stores. Their bottoms are often already bulging outward, which is in itself a sign of a potentially serious hazard. If you need to transfer hydrogen peroxide into a safety bottle, make absolutely certain that the receiving bottle is perfectly clean. Before filling it, test it by rinsing its inner walls with a small amount of hydrogen peroxide to ensure that no unexpected gas evolution occurs as a result of any residual contamination.

Aqueous ferric chloride solution does not keep well in a glass bottle, which eventually becomes stained by a deposit that cannot be removed. This phenomenon does not occur in HDPE bottles.

Certain highly flammable organic solvents whose vapors are explosive, such as diethyl ether, can certainly be stored in glass bottles fitted with caps incorporating a PTFE liner. Nevertheless, because of the risk of breakage, it is sometimes preferable to store such solvents in aluminum bottles fitted with a special white PVC cap lined internally with an aluminum insert. Such bottles can be purchased from specialized laboratory suppliers or may sometimes be obtained from hairdressers or perfume shops.

Many solid chemicals are sensitive to atmospheric moisture and gradually undergo chemical change. Sodium sulfite, for example, is slowly converted into sulfate. For this reason, I recommend storing such substances only in HDPE bottles fitted with caps containing an internal foam liner that provides a better seal. An even tighter seal can be obtained by covering the mouth of the bottle with a piece of plastic food wrap before screwing on the cap, so that the film becomes compressed within the threads of the closure.

Some solid chemicals, such as aluminum chloride or powdered magnesium, are so sensitive to moisture and so liable to react with it that they are better stored in narrow-neck glass bottles intended for liquids and fitted with caps incorporating a PTFE liner. Also particularly well suited for these substances are certain pharmacy bottles fitted with a metal cap that can be secured over a plastic septum (Figure 35).

In summary, the storage of chemicals and chemical elements must always take into account the individual properties of each substance in order to determine the most appropriate storage method and to keep incompatible materials well separated. This precaution is necessary not only in the event of accidental breakage of two containers, but also because vapors may gradually escape from containers that are not perfectly airtight. Let there be no misunderstanding: no bottle is perfectly airtight.

1.2.16 Practical Tips from the Past

I readily admit that I have drawn much inspiration from older authors, something that may surprise modern chemists accustomed to equipment very different from that of earlier times. Yet it is precisely in old books that one can find countless practical tricks and ingenious solutions that modern authors generally fail to mention—or quite simply no longer know.

Over the course of my reading, certain authors naturally impressed me more than others by their obvious experimental skill. One of them, Professor Deluc, once devised a portable laboratory containing everything necessary to perform a multitude of highly instructive experiments. In his book *La Chimie pour Tous*, published in 1880, this remarkable educator—now completely forgotten—described practical methods that appeared to be entirely unknown to many of his distinguished contemporaries. Here is one example...

When preparing nitric acid in the laboratory, one is confronted with the evolution of large quantities of toxic gases. Yet few schools or small laboratories possess the powerful and expensive fume hoods that alone are capable of removing such gases without rapidly suffering corrosion themselves. Professor Deluc therefore proposed an extremely ingenious system (Figure 38). The distilled acid flowed into a graduated cylinder floating in a water trough and enclosed within a glass tube open at the bottom and closed at the top. The gases escaping together with the liquid from the condenser were thus forced to come into contact with the water contained in the tube, displacing it while simultaneously dissolving in it. In this way, they immediately lost their toxicity. To eliminate all danger from this experiment, it is therefore sufficient to transpose this schematic arrangement to modern laboratory equipment.

In Professor Deluc's drawing, one may also observe twisted metal wires used to hold the apparatus in position. Here again there are valuable lessons for amateurs, who

do not always possess sophisticated equipment including numerous clamps and sturdy professional support stands.

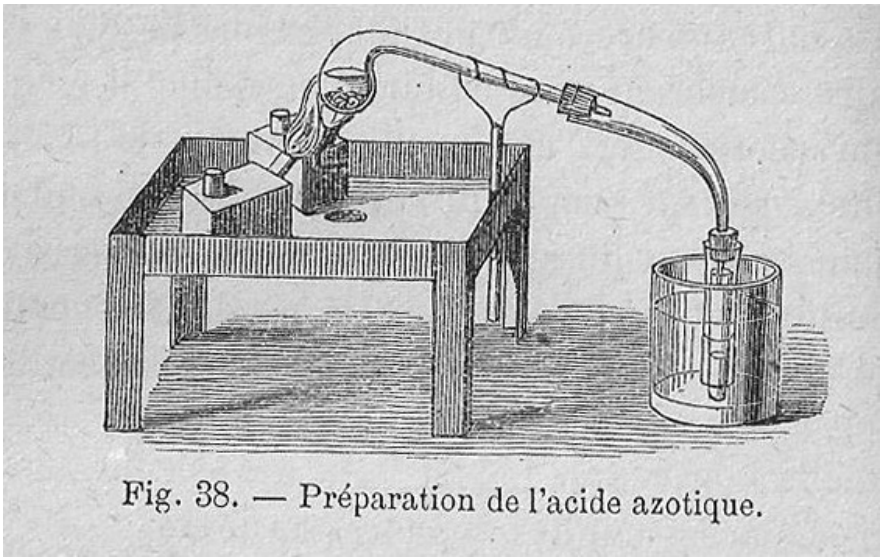


Figure 38

When it is desired to bubble a gas through a liquid, the usual choice is a Drechsel bottle (mentioned earlier). Professor Deluc, however, preferred the simple U-tube for two reasons. The first was that a U-tube provides more vigorous agitation of the liquid and therefore better contact between the gas and the liquid. The second was that, at the end of an experiment, when gas production ceases, the gas may sometimes dissolve or react with the liquid through which it has been bubbling. This can create a partial vacuum capable of drawing the liquid back out of the Drechsel bottle, with potentially troublesome or even dangerous consequences. This danger is completely eliminated when a U-tube is used, since even if the liquid is drawn back towards the reaction flask, it can never rise far enough to enter it.

ABOUT THIS CHAPTER

The purpose of this chapter has not been to present every item of laboratory equipment that exists, for such a task would require an entire book in itself. Rather, the objective has been to familiarise the reader with the principal categories of equipment most frequently encountered in amateur chemistry, while drawing attention to their advantages, limitations, and practical applications.

As we shall see in the following chapters, successful experimental work depends less upon the quantity of apparatus available than upon understanding its proper use, its limitations, and the precautions required for safe operation.

Chapter 2 - A Little Pedagogy...

Although chemistry is a fascinating subject, it attracts surprisingly few students in secondary schools. The reason is simple: like physics, it is often taught in a dry and uninspiring manner, giving students the impression that it is an almost entirely theoretical science, somewhat like mathematics. Far too few experiments are demonstrated and explained from a genuinely practical standpoint, and among those that are shown, only a handful are truly captivating. Distilling water in which a few cloves have been crushed is hardly likely to interest teenagers, who would much rather turn to YouTube to discover—and often feel tempted to imitate—far more spectacular demonstrations.

Before going any further, I would therefore like to present a few examples illustrating the kind of approach a teacher should adopt in order to make chemistry genuinely engaging. Young people want to see experiments that are surprising, spectacular, or puzzling—experiments that reveal things they did not previously know. They enjoy being astonished, and therein lies the secret of good teaching. Their perfectly legitimate expectations should therefore be met by carefully selecting demonstrations that will capture their attention and serve as a starting point for teaching concepts that will no longer appear tedious, but rather enriching and closely connected to everyday life and concerns.

2.1 Demonstration Experiments

First Experiment

This experiment allows students to discover both alcoholic fermentation and fractional distillation, the latter providing an excellent introduction to the principles underlying petroleum cracking. The first stage is extremely simple. A one- or two-litre Erlenmeyer flask is filled with a strongly sugared aqueous solution into which baker's yeast, readily available from any supermarket, is added. The flask is closed with a stopper fitted with a safety funnel containing one or two bulbs. The

Erlenmeyer flask should be filled fairly high, since alcoholic fermentation is an anaerobic process. Nevertheless, sufficient space must be left beneath the stopper because a layer of foam generally forms on the surface.

Yet within a few minutes the students will observe the yeast settling at the bottom of the flask while small bubbles begin rising along the walls. Their attention should be drawn to the limewater placed in the safety funnel. It first turns cloudy and then, after a time, gradually becomes clear again as HCO_3 causes the calcium carbonate to dissolve.

This secondary observation, which can be used to explain the formation of caves, stalactites, and stalagmites, may also be performed separately using a simple apparatus that allows carbon dioxide to bubble through limewater. It also provides an opportunity to demonstrate that human respiration produces carbon dioxide. Students can easily verify this by blowing through a simple cocktail straw into a vessel containing limewater.

After a few days, the students should be invited to smell the contents of the flask. They will clearly detect the characteristic odour of alcohol. This is the ideal moment to proceed with the distillation. A very simple distillation apparatus may be used. If a Vigreux column is available, it becomes easy to demonstrate that the most volatile components rise first through the column while the less volatile fractions condense and return downward. An excellent teaching aid is to colour the fermented liquid before distillation, showing that only colourless vapours rise initially. Several successive fractions of the distillate may then be collected. Students can sample these fractions by touching them with a fingertip or, for better hygiene, by using disposable cocktail sticks. If only a simple distillation apparatus without a fractionating column is available, the droplets emerging from the condenser can be sampled at different stages of the operation. By taste alone, students quickly realise that the alcohol concentration decreases steadily as distillation proceeds.

Since this lesson necessarily unfolds over several days, it may also be combined with a biological study. If one or more microscopes are available, a small quantity of yeast diluted in water can be examined microscopically. Cooperation between chemistry and biology teachers may even be considered.

Second Experiment

This experiment demonstrates that two hazardous substances can combine to produce a new substance that is essentially harmless.

A shallow porcelain evaporating dish or a borosilicate glass dish (Pyrex type) is used. Concentrated hydrochloric acid is poured into the dish, after which a small quantity of solid sodium hydroxide pellets is added all at once. Care must be taken to ensure that the hydrochloric acid remains in excess. The reaction is vigorous and

strongly exothermic, something the students can readily observe. A cloud of vapour immediately rises from the dish, and the heat generated generally drives off the acidic fumes. As a precaution, however, the resulting white, moist mass should be diluted with a little water and then brought to a boil before the liquid is evaporated to dryness. The residue is diluted a second time, and the pH is checked to confirm that no dangerous alkalinity or acidity remains. The resulting solution can then be tasted. It has become ordinary salt water, a flavour that everyone immediately recognizes.

The same experiment can, of course, be carried out using hydrochloric acid and sodium hydroxide solutions delivered slowly, drop by drop, from burettes into a flask equipped with a pH indicator or pH-measuring device. The addition is stopped when the acidity measurement confirms that hydrochloric acid remains in slight excess.

Although this version is far less spectacular than the previous one, the ideal approach is naturally to perform both demonstrations.

Third Experiment

A fairly large funnel is placed beside the flame of a Bunsen burner supplied with methane (natural gas). The funnel is connected to a suction pump.The gas drawn into the funnel is passed through a Drechsel bottle containing limewater. The limewater rapidly turns cloudy owing to the formation of carbon dioxide during the combustion of methane.

This simple experiment provides a convenient opportunity to explain why some governments seek to limit or even eliminate domestic heating systems fuelled by natural gas. The carbon dioxide released by such combustion is generally considered to be one of the factors contributing to global warming and climate change.

Fourth Experiment

Here is an experiment that fascinates many budding chemists despite being relatively simple to perform.

A large test tube or a small flask is first cleaned thoroughly with a detergent containing a little ammonia and then rinsed with distilled water. The objective is to obtain a glass surface that is as clean and grease-free as possible. One gram of silver nitrate is dissolved in 40 ml of water inside the perfectly cleaned vessel. A dilute aqueous ammonia solution is then added drop by drop while the mixture is stirred continuously with a magnetic stirrer. At first, a precipitate forms, turning the liquid a dirty brown colour. The experimenter's skill lies in stopping the addition of ammonia at the precise moment when this precipitate has just completely

disappeared and the solution has once again become perfectly clear.

DISTILLED OR DEMINERALISED WATER?

Large supermarkets and hardware stores now commonly sell containers of water labelled either "distilled" or "demineralised." It should be understood that these products are generally nothing more than demineralised water and not true distilled water, whose production is considerably more expensive.

Although the demineralisation processes used are entirely adequate for applications such as steam irons, windscreen-washer reservoirs, or lead-acid batteries, this water is unsuitable for laboratory use and should be avoided for that purpose. The least expensive demineralised water suitable for laboratory work can often be obtained from pharmacies, where regulations require the use of particularly neutral water. It may be stored either in glass carboys or in food-grade white PVC containers.

Genuinely distilled or double-distilled water is required only for certain specialised professional laboratory applications and should then be stored in appropriate containers.

At this stage, an ammoniacal silver nitrate solution has been obtained. After magnetic stirring has been stopped, one or two drops of diluted formaldehyde (or glucose) solution are added. The vessel is immediately shaken briefly by hand and then placed without delay in a water bath maintained at approximately 35°C. As if by magic, a brilliant silver mirror forms over the inner surface of the vessel, creating a reflective coating in which everyone can admire their own image. The more slowly the reaction proceeds, the more beautiful the mirror will be. For this reason, excessive amounts of formaldehyde should be avoided.
Safety note: Ammoniacal silver solutions should be prepared immediately before use and never stored. With time they may form unstable compounds. The solution should therefore be used promptly and disposed of appropriately once the demonstration has been completed.

WHAT DOES "UNSTABLE" MEAN?

Throughout this book, reference will occasionally be made to substances described as unstable. What exactly does this mean?

In the most favourable cases, it simply means that the substance slowly changes into another, entirely different substance without creating any danger. In less favourable circumstances, however, an initially harmless substance may gradually transform into one that is extremely dangerous and may even become capable of spontaneous explosion.

Fifth Experiment

This experiment demonstrates that hot acetic acid vapours are flammable.

The demonstration is usually performed by heating a small quantity of acetic acid in a test tube and igniting the vapours with a match. There is, however, a way to make the experiment considerably more striking.

A few millimetres of acetic acid are placed in a borosilicate 3.3 evaporating dish. An epiradiator is positioned a short distance above the liquid surface. Under these conditions, the vapours ignite spontaneously with a slight popping sound solely as a result of the radiant heat. No flame or spark is required. The centre of Figure 39 shows the precise moment of ignition.

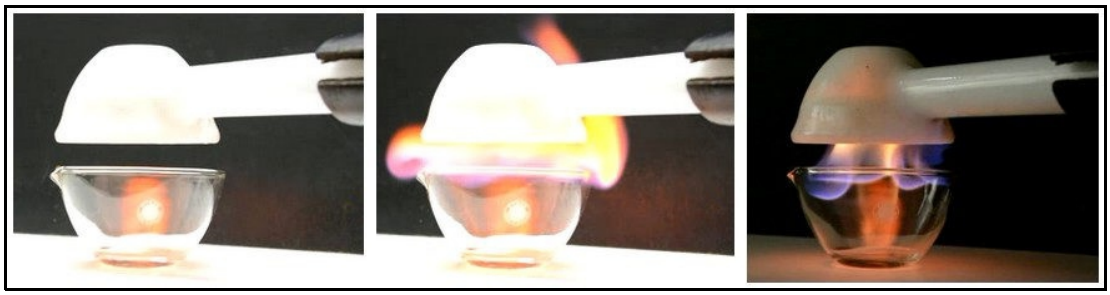


Figure 39

The demonstration provides an excellent reminder that certain substances commonly regarded as non-flammable liquids may nevertheless produce highly flammable vapours once these vapours reach a sufficiently hight temperature.

Sixth Experiment

In chemistry, words can sometimes be misleading. A good example is provided by the so-called acid carbonates and neutral carbonates of the alkali metals.

The demonstration is straightforward. A solution of sodium carbonate (Na_2CO_3) is placed in a small beaker on the left, while a solution of sodium hydrogen carbonate (sodium bicarbonate, $NaHCO_3$) is placed in an identical beaker on the right. A drop of phenolphthalein solution is added to each.

The solution containing the so-called neutral carbonate develops a much stronger red coloration and is therefore distinctly more alkaline than the solution containing the acid carbonate. Accurate pH measurements confirm that both salts produce alkaline solutions, but that the alkalinity is considerably greater in the case of the so-called neutral carbonate.

Seventh Experiment

This experiment requires some theoretical background before it can be fully understood. It is therefore best presented, at the appropriate stage of instruction, as a challenge to the students: "Can you explain what is happening?"

A few fragments of marble are placed in sulfuric acid diluted with an equal volume of water. After a brief evolution of carbon dioxide, the reaction comes to a halt because insoluble calcium sulfate forms a protective barrier around the marble. A few pieces of calcium chloride are then added. The reaction starts again—slowly, but this time continuously.
Explanation: $H_2SO_4+CaCl_2 \rightarrow CaSO_4+2HCl$. The hydrochloric acid produced then reacts with the marble: $CaCO_3+2HCl \rightarrow CaCl_2+CO_2+H_2O$. Calcium chloride is therefore continuously regenerated. As long as sulfuric acid remains present, the reaction can continue.

Eighth Experiment

This is the well-known demonstration commonly referred to as the "Blue Bottle Experiment." It is quite simple to perform.

Any colourless glass bottle that can be tightly sealed may be used. The container should have a capacity three to four times greater than the volume of liquid employed. A one-litre bottle is generally ideal, both because of its size and because it allows a large audience to observe the reaction clearly. Begin by pouring 250 mL of water into the bottle. Dissolve 3 g of dextrose followed by 5 g of sodium hydroxide or potassium hydroxide. Before sealing the bottle, add a very small spatula-tip quantity of methylene blue powder. The bottle is then closed and shaken vigorously. The liquid immediately turns blue. The colour does not persist, however. Gradually it fades, sometimes passing through a pinkish tint, until the solution once again becomes colourless.

If the bottle is shaken again, the blue colour immediately returns—only to disappear once more after a short time. This cycle may be repeated many times. Eventually the effect ceases. When this occurs, simply open the bottle, allow a little fresh air to enter, close it again, and shake. The blue coloration reappears immediately. This clearly indicates that atmospheric oxygen plays an essential role in the reaction. The process is not, of course, perpetual.

Ninth Experiment

A related but somewhat more demanding demonstration may also be performed. English-speaking chemists often refer to it as the "Chemical Traffic Light."

A 500 mL flask that can easily be sealed and shaken is used. Into it are poured 200 mL of distilled water heated to approximately 50°C and a small spatula-tip quantity of indigo carmine, sufficient to produce a deep blue solution. A spoonful of glucose is then added and the mixture stirred until complete dissolution has occurred. Finally, 50 ml of water containing a small quantity of sodium hydroxide is added. A remarkable sequence of colour changes follows. The solution passes from blue to violet, then to green, red-orange, and finally yellow.

The flask is then sealed and shaken vigorously. The liquid immediately returns to green before once again changing to yellow through intermediate orange shades.

The reaction can be repeated several times, although only for a relatively short period because the dye is gradually consumed.

The experiment may also be carried out on a heated magnetic stirrer, as shown in Figure 40. The difference in liquid level between the beakers results from the rotation speed of the magnetic stirring bars, which causes the liquid to rise along the walls. When stirring stops, the liquid therefore returns to its original level.

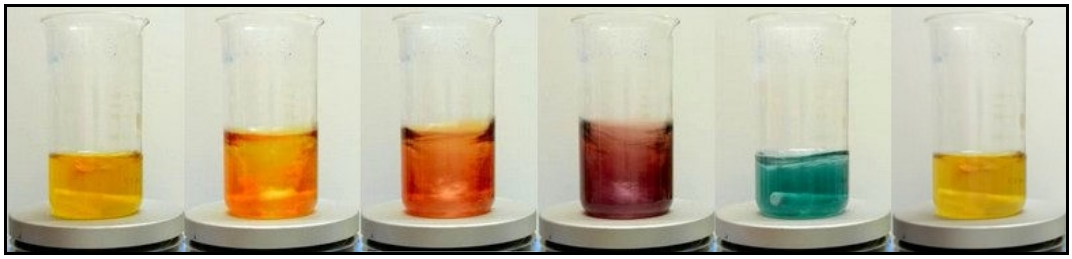


Figure 40

Careful observation of the flask reveals that, during agitation, the colour change begins at the surface where the liquid is in contact with the atmosphere (Figure 41). As in the previous experiment, atmospheric oxygen is therefore essential to the reaction.

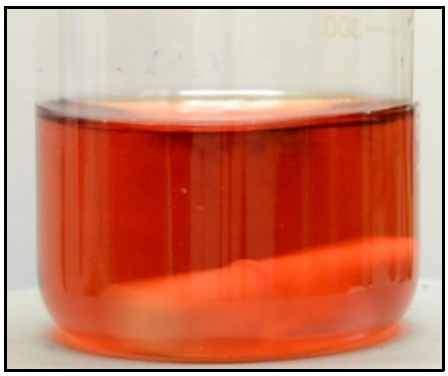


Figure 41

Tenth Experiment

Using the analytical classification proposed by Denigès and his collaborators in their *Précis de chimie analytique* (Paris, Maloine, 1930), a series of attractive demonstration experiments can be devised using a few common metals.

The metals are first treated with hydrochloric acid, either cold or hot, depending on what is required to make them react. Two outcomes are then possible: either a

coloured solution is obtained or the solution remains colourless. If the solution is coloured, it is boiled for some time in order to remove a substantial portion of the excess acid. After that, ammonia in excess is then added. The following results may be observed:
Cobalt: A yellowish solution that gradually browns on exposure to air
Nickel: A blue solution
Iron: A pale greenish-white precipitate that yellows on exposure to air
Chromium: A violet or lilac flocculent precipitate

These simple reactions provide useful illustrations of qualitative analytical chemistry.

Eleventh Experiment

A glass tube approximately 4 cm in diameter and about 60 cm long is used. The tube is divided into three sections of roughly 20 cm each by inserting two plugs of glass wool, one impregnated with a potassium bromide solution and the other with a potassium iodide solution. Each plug is therefore situated approximately 20 cm from the stopper placed at either end of the tube.

Chlorine gas is then passed through the tube in the direction KBr → KI while gentle heat is applied near the potassium iodide plug. Beyond the first plug, the characteristic reddish colour of bromine appears. Beyond the second, violet iodine vapour is produced and deposits as fine crystals on the inner wall of the tube. Any excess chlorine leaves through the far end of the apparatus.

This experiment provides an elegant visual demonstration of the relative chemical activity of the halogens.

Twelfth Experiment

This demonstration requires two identical Drechsel bottles, each having a capacity of approximately 100 ml. The first contains about 3 cm of concentrated ammonia solution and the second an equal depth of concentrated hydrochloric acid.

The outlet tubes of both bottles are connected by flexible tubing to a Y-tube whose third branch leads as directly as possible into a vertical glass tube approximately 3 cm in diameter. The upper end of this tube is constricted so that its opening measures only about 2 cm across.

The inlet tubes of the two Drechsel bottles are connected to a second Y-tube, whose third branch is attached by flexible tubing to a one-way aspirating and blowing rubber bulb of the type commonly used in spray devices. The bulb is firmly squeezed three or four times. Equal quantities of air are forced through both Drechsel bottles,

carrying the vapours into the vertical tube where a dense white cloud immediately forms. With a little practice—and by controlling both the rhythm and pressure applied to the bulb—the cloud can be made to emerge from the tube as rings or mushroom-shaped puffs of smoke (Figure 42).

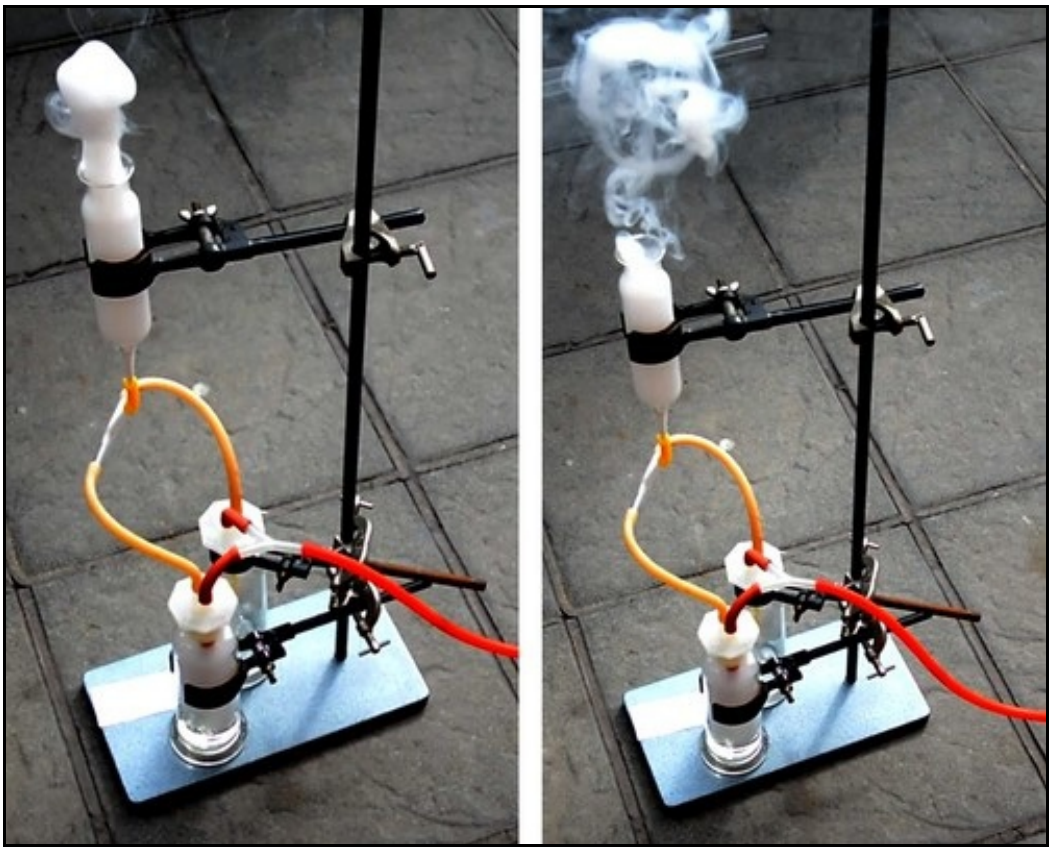


Figure 42

Because this demonstration produces a considerable quantity of irritating fumes, it should be performed outdoors or in a very well-ventilated area.

Thirteenth Experiment

Six test tubes are prepared. Into each is poured, to a depth of approximately 3–4 cm, a solution of a different metallic salt: cobalt chloride, nickel sulfate, copper sulfate, manganese chloride(II), ferric chloride(III), and zinc sulfate. A solution of borax (sodium tetraborate), slightly warmed to facilitate dissolution, is then added to each tube. A precipitate forms in every case. With cobalt ions it is lilac; with nickel ions, pale green; with copper(II) ions, blue; with manganese(II) ions, white; with iron(III) ions, reddish-brown; and with zinc ions, white.

The contents of all six test tubes are then brought to the boil.

The tube containing cobalt ions changes from lilac to violet and then blue, before returning to lilac upon cooling. The tube containing copper ions changes from blue

to pale green, after which the precipitate rapidly settles as a fine powder. The manganese-containing tube develops a yellowish tint. In the tube containing iron(III), the precipitate dissolves and the liquid becomes more intensely red. No significant change is observed in the tubes containing nickel and zinc.

Further transformations occur when concentrated ammonia solution is subsequently added to each tube. Depending upon the metal present, colour changes are observed and, in some cases, the precipitate disappears completely.

Naturally, the experiment may be extended to include other metallic salts

2.2 Pseudo-Alchemy

Throughout the centuries, alchemy and alchemists have inspired countless dreams and fantasies. A lecturer can easily captivate an audience by addressing this subject while at the same time providing an opportunity to retrace, in broad outline, the history of chemistry.

Contrary to what is often claimed, chemistry came first. Long before alchemy appeared, numerous discoveries had already been made in the fields of metallurgy (tools and weapons), pigments and dyes (body paints, frescoes, and textile colouring), and even food preparation through the cooking of various substances.

Alchemy emerged later as an imperfect branch of chemistry, combining practical experimentation with philosophical and mystical speculation. Through their investigations, certain alchemists rendered valuable services to chemistry by discovering a number of important substances. Unfortunately, their methodology and preconceived ideas condemned them to theoretical stagnation. In a sense, it was Lavoisier who dealt the decisive blow to alchemy.

The following experiments illustrate some of the tricks once employed by alchemists to impress or deceive their audiences.

Take a small copper coin—or any small copper object—and clean it with acetic acid. Rinse it thoroughly and then degrease it with aceton or ether so that no trace of grease remains. From this point onward, avoid touching the coin with your fingers. Place a few grains of sodium hydroxide and a small quantity of zinc powder in a shallow dish and heat gently until the zinc begins to react. Immediately immerse the object in the mixture. After a few seconds, remove it and rinse it. The object is now coated with a brilliant layer of zinc and is virtually indistinguishable from a silver one. If it is then heated gently for a short time, it appears to transform into gold. In reality, a thin layer of brass has formed on its surface.

A similar demonstration may be performed as follows...

Prepare a precipitate of silver chloride by mixing a solution of silver nitrate with a solution of sodium chloride. Remove the liquid phase and dissolve the precipitate in a solution of sodium thiosulfate. A small copper object, previously cleaned and degreased, is then immersed in this solution. In less than a minute, it becomes coated with a layer of genuine silver. The object should then be rinsed and dried in an atmosphere free from hydrogen sulfide, which would quickly tarnish the silver coating and turn it black.

Here is a final experiment of the same kind, even simpler than the preceding ones. A heavily tarnished copper object (a European coin, for example) is immersed in an aqueous solution of sodium cyanide. The object rapidly regains its original appearance (Figure 43).

Figure 43

Safety note: Sodium cyanide is an extremely toxic substance. The purpose of this experiment is merely to illustrate a chemical cleaning process and not to encourage the preparation, use or storage of alkaline cyanides for any other purpose.

It goes without saying that these apparent "transmutations" are often quite effective at surprising spectators, especially if only part of the object's surface is treated.

2.3 Diffusion and Cyclic Reactions

A particularly attractive experiment is the following.

- A test tube is filled to about three-quarters of its height with a fairly dilute solution of sulfuric acid. A few drops of phenolphthalein dissolved in alcohol are then added. The liquid remains perfectly colourless. Using a pipette, a moderately concentrated ammonia solution is carefully layered on top of the acid solution. Since ammonia solution is significantly less dense than the sulfuric acid solution, it remains in the upper part of the test tube, where it reacts with the phenolphthalein and produces a coloured ring. The tube is then stoppered and left undisturbed. Gradually, the coloured ring fades and eventually disappears because the ammonia slowly diffuses into the sulfuric acid solution, where neutralisation takes place (Figure 44).

Figure 44

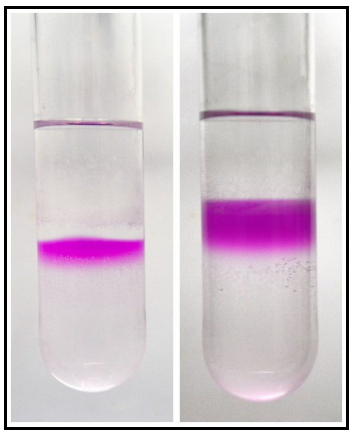


Figure 45

- Another attractive diffusion experiment may be performed using various colour indicators. I shall mention only one example. A test tube approximately 3 cm in diameter is filled to a depth of about 3 cm with a saturated solution of sodium chloride. An equal depth of approximately 90% ethyl alcohol is then carefully poured on top. A few drops of an alcoholic phenolphthalein solution have previously been added to the alcohol. The two liquids remain separated and form distinct layers. A few grains of sodium hydroxide are then dropped into the test tube. These pass through the alcohol layer and settle at the bottom of the tube. As the hydroxide gradually diffuses through the salt solution, a coloured ring appears and slowly expands over the course of several hours (Figure 45). This experiment provides a particularly clear visual demonstration of the progressive diffusion of a substance through a liquid medium.

- Another particularly attractive experiment may also be performed. A Petri dish lid is placed on a perfectly horizontal surface. A small quantity of distilled water is poured into it, just sufficient to cover the entire bottom with a very shallow layer. Near one edge of the dish, a pea-sized quantity of lead nitrate is placed. At the opposite edge, a similar quantity of potassium iodide crystals is introduced. Before long, a curved yellow boundary line appears between these two "poles." The line is noticeably closer to the lead nitrate than to the potassium iodide.
The explanation is straightforward. Potassium iodide dissolves more readily and therefore diffuses more rapidly through the water. As a result, the zone where the two substances meet and react is displaced toward the more slowly diffusing lead nitrate.
This experiment provides a particularly clear illustration of how differences in diffusion rates can influence the location and shape of a reaction front.

- A few drops of a suitable colour reagent (see further on) are added to a warm aqueous solution of gelatin, which is then poured into a Petri dish or any shallow vessel with a flat bottom. Once the gelatin has solidified, drops of either an acidic or an alkaline substance are placed on its surface. Coloured or decolourised circles then appear and slowly expand as the substance gradually penetrates the gelatin (Figure 46).

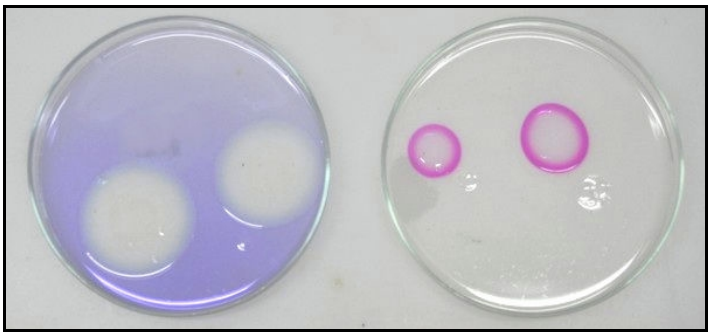


Figure 46

The experiment provides a remarkably clear visual representation of the way one substance diffuses through another.

- The same type of demonstration may be carried out using substances that react together to form precipitates. As early as 1885, it was discovered that the diffusion of such precipitates often occurs in the form of concentric waves. Beginning in 1901, Stéphane Leduc showed that these diffusion fields could be either monopolar or bipolar and that they displayed properties closely resembling those of magnetic or electrical fields, particularly with regard to the attraction of opposite poles.
He further observed that, much like wave phenomena, these diffusion fields could be refracted when passing through prisms. He also demonstrated that narrow openings could generate new diffusion-wave sources in exactly the same way that diffraction phenomena are observed with sound or light waves. (Albert and Alexandre Mary, *Dictionnaire de biologie physiciste*, Paris, Maloine, 1921, articles "Diffusion" and "Periodicity".)
One way to observe these phenomena is to produce what are known as Liesegang rings. nce again, two substances are selected that react together to form coloured precipitates. solution of the first substance is prepared in a test tube and heated to boiling with agar-agar. Unlike gelatin, agar-agar does not produce foam and ultimately forms a firm gel. The tube is then left undisturbed overnight. The following day, once gelation is complete, a diluted solution of the second substance is carefully poured onto the surface and the tube is closed with a stopper that exerts slight pressure on the solid gel. The two substances react first at the surface and then progressively deeper within the gel, producing a series of periodic rings. These rings indicate that a form of periodicity or rhythmic waves develops within the reaction itself.
The example shown in Figure 47 was obtained by pouring an ammonia solution onto a gelled solution of nickel sulfate.

Figure 47

- There is yet another way to illustrate the periodic nature of certain physicochemical phenomena. Here is an experiment particularly easy to perform. A mixture is prepared from 9 ml of ethyl alcohol and 9 ml of concentrated sulfuric acid. The acid must be added very slowly to the alcohol while stirring continuously and cooling vigorously. The mixture is then poured into a porcelain evaporating dish containing 5 g of benzoic acid. Moderate heating is applied while the contents are stirred continuously with a glass rod. Once all the benzoic acid has disappeared and the liquid has acquired a faint brown colour, heating is discontinued. The dish is then allowed to cool slowly in a location free from vibration and dust. At first, white vapours will probably be given off, but these soon disappear. Later, once

crystallisation is complete, the contents of the dish develop a pleasant fragrance and a close examination reveals that crystallisation has taken place in the form of concentric waves radiating outward from the centre—rather like the growth rings of a tree trunk. Along these circles, the material is also arranged in a distinctly periodic fashion (Figure 48).

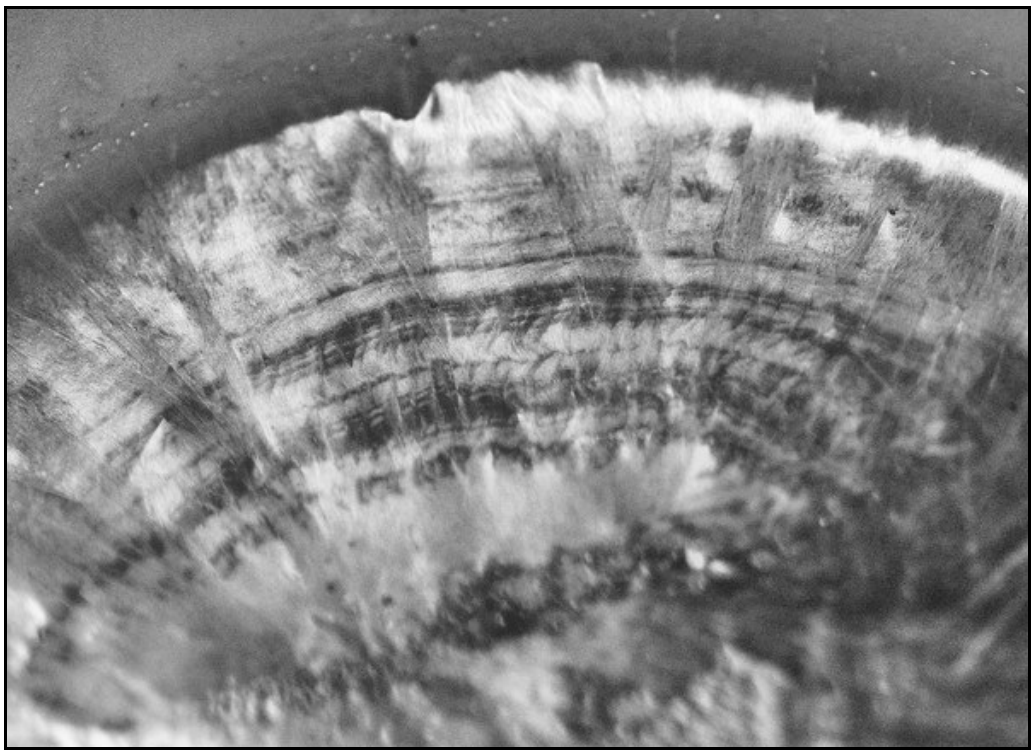


Figure 48

2.4 Osmosis and Surface Tension

The time has now come to say a few words about osmosis.

- This phenomenon can easily be demonstrated using very simple equipment. All that is required is a fabric whose weave is sufficiently tight to impede, at least initially, the passage of water. A cylindrical funnel is fitted with a piece of damp cloth stretched tightly across its upper opening and held in place with an elastic band. The cylindrical portion of the funnel is then filled with a concentrated sugar solution up to the beginning of the neck. The funnel is subsequently inverted and immersed in a beaker of water.
Alongside this arrangement, the reverse experiment may be performed by filling the cylindrical portion of a second funnel with water and then immersing it in a beaker containing a sugar solution.
The rise or fall of the liquid level within each funnel can readily be observed, providing a simple visual demonstration of osmotic processes such as those occurring in plants.

- To these experiments may be added another illustrating the effects of surface tension. A Petri dish approximately 5 cm in diameter is placed on a perfectly horizontal surface and a drop of mercury is introduced into it. The mercury is then completely covered with a layer of dilute nitric acid (between one-eighth and one-tenth strength). A quantity of potassium dichromate, preferably in the form of a single large crystal, is then added to the liquid. Chromic acid is formed and, as it diffuses through the solution, modifies the surface tension at the interface with the mercury droplet. The mercury consequently changes shape and extends pseudopod-like projections in a manner reminiscent of the movements of an amoeba. For this reason, the experiment was once known as the Mercurial Amoeba (See also page 263 for more explanations).

2.5 Mineral Gardens

What have sometimes been called mineral gardens constitute one of the most easily reproduced outcomes of a series of experiments popularised by the French biologist Stéphane Leduc (1853–1939).

Contrary to what has occasionally been written, Leduc never sought to create life artificially. His objective was rather to understand the physicochemical laws that might govern the origin and growth of living organisms. Through a large number of experiments based principally on osmotic phenomena, Leduc developed a variety of methods capable of producing mineral growths whose external forms resembled plants, small animals, and even certain stages of cell division.

The various procedures employed by Leduc may be summarised quite simply. They consisted essentially in producing precipitates that developed through successive budding processes within a suitable medium. By varying certain factors, such as the density of that medium, he was able profoundly to modify the form assumed by these osmotic growths.

Here are a few examples of such chemical growths, all of which can be produced with very modest equipment.

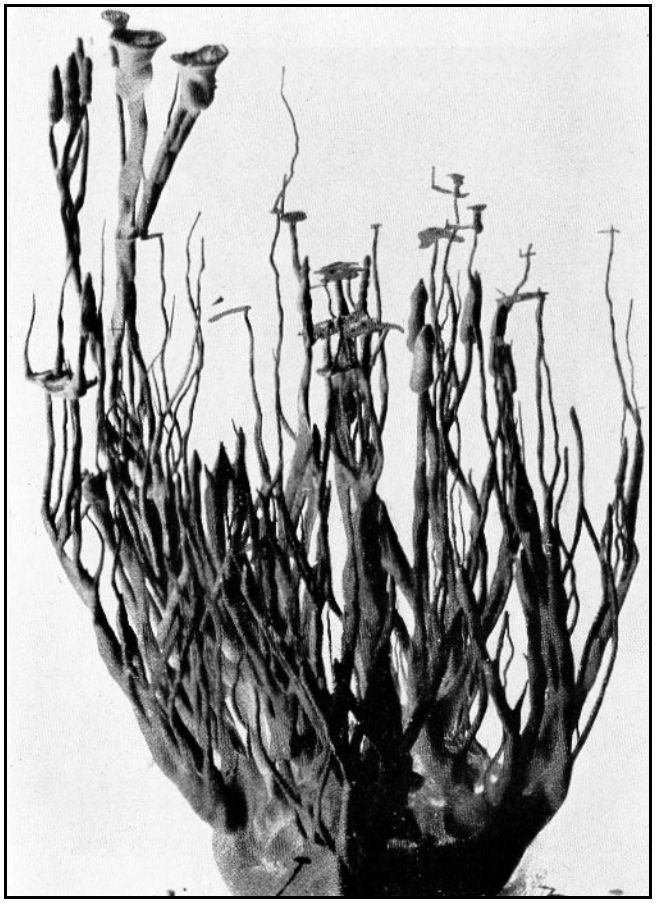
- A solution of sodium silicate is prepared at various concentrations and poured into tall containers resembling wide test tubes or high-form beakers. Into these vessels are dropped fairly large crystals of different salts such as copper sulfate, potassium ferrocyanide, nickel sulfate, ferrous sulfate(II), cobalt chloride, manganese chloride, potassium permanganate, or ferric chloride(III). The crystals must be large enough to sink readily to the bottom of the vessel rather than remain floating on the surface. Leduc sometimes coated slightly moistened crystals with powdered sugar so that they would reach the bottom of the vessel before coming into direct contact with the solution. Once immersed in the silicate solution, the crystals become coated with a coloured membrane consisting of a precipitate. This membrane possesses the

characteristics of an osmotic membrane. It gradually absorbs water while the crystal dissolves within it, causing the membrane to swell progressively. Eventually the swelling becomes sufficient to rupture the membrane. A small quantity of dissolved salt escapes and immediately becomes enclosed within a new osmotic membrane attached to the first. Then the process repeats itself. Outgrowth after outgrowth, the crystal produces a structure that either rises upward or spreads laterally, depending upon density differences within the silicate solution. In most cases, irregular stems are formed, although flattened shell-like structures may also appear. Each salt crystal produces its own characteristic type of coloured growth. If several different crystals are introduced into the same vessel, structures of different colours develop simultaneously, creating the appearance of a miniature mineral garden or forest.

Another method consists in bringing together salts of which one is protected by a kind of syrupy coating. For example, a sugar syrup containing a small quantity of potassium ferrocyanide may be prepared and droplets of this syrup allowed to fall into a copper sulfate solution.

To produce beautiful and convincing results, Leduc's experiments require a certain degree of skill together with a fairly large number of trials in which various parameters—among them the concentration of the sodium silicate solution—are systematically varied.

Time and patience are therefore essential if one wishes to master the experimental conditions necessary for obtaining attractive osmotic growths.



A "mineral garden" obtained by Stephane Leduc (Taken from : *La biologie synthétique*, Paris, Poinat, 1912)

Chapter 3 - Colour Indicators and Reagents

3.1 Colour Indicators

Colour indicators are substances of relatively complex composition that change colour according to the pH (degree of acidity or alkalinity) of the liquids with which they are mixed. This phenomenon is known as a colour change or transition.

Some of these substances have long been available in the form of dry test papers, such as litmus paper or phenolphthalein paper. For many years, however, the chemical industry has also produced plastic test strips containing several coloured zones impregnated with different indicator substances. These modern strips provide measurements that are considerably more precise than the traditional indicator papers of the past.

The following are a few examples of colour indicators commonly used in solution.

Red Cabbage Juice — Many chemistry teachers and amateur experimenters use red cabbage juice in place of litmus tincture or litmus paper. It can be prepared by boiling shredded red cabbage in water and filtering the resulting purple liquid. A tincture may also be obtained by crushing the cabbage in alcohol. In either case, the preparation does not keep well and must be used relatively soon after it is made. Although inexpensive, it is therefore not a particularly practical long-term indicator. It remains, however, an excellent teaching aid and provides a useful link between chemistry and everyday cooking, where vinegar or baking soda may be used to alter the colour of red cabbage.

Privet Berry Juice — Crush a few privet berries in a porcelain mortar, add a small quantity of water, and filter the resulting reddish-purple juice. A few drops added to an acidic solution produce a pinkish-red colour. In contrast, a strong alkali such as sodium hydroxide produces a green colour that gradually turns yellow after a few minutes. Like red cabbage juice, privet berry juice cannot be stored for long periods.

Elderberry Juice — Crush ripe black elderberries with a pestle in the presence of

a small quantity of water. Bring the mixture to the boil and then filter it. A cherry-red liquid is obtained. The filter papers used in the process dry to a red-violet colour. When such paper is exposed to ammonia gas, it turns duck blue. The liquid extract behaves similarly in the presence of other alkaline solutions such as sodium hydroxide. In acidic solutions, however, the colour changes to magenta red. The juice may therefore also be used as a pH indicator, although unfortunately it keeps no better than most other plant extracts.

Brazilwood (Pernambuco Wood) — Place small pieces of Brazilwood in a flask with water. Heat for approximately thirty minutes, adding water as necessary to compensate for evaporation, and then filter the liquid. A predominantly red solution is obtained. Sulfuric acid produces little or no visible effect. Hydroxides, however, give rise to a very intense crimson-red coloration. Attention should be paid to the fact that the solution deteriorates upon exposure to light and that the colours produced by hydroxides are not permanent.

Violet Syrup — This inexpensive indicator, which behaves somewhat like litmus and red cabbage juice, is seldom used today. The syrup, which naturally contains sugar, keeps very well and is commercially available ready for use. It is violet in colour, turns red in acidic solutions, and green in alkaline ones. Before use, it should be diluted slightly with distilled water.

Cochineal Carmine — Cochineal carmine is a food colouring (E120) derived from an insect, its principal constituent being carminic acid. To prepare it, place a small spatula-tip quantity of cochineal carmine in a 50 mL beaker one-third filled with water and stir. Add a few drops of the resulting solution to hydrochloric acid. The liquid rapidly develops a yellow colour. Repeat the experiment with a solution of sodium hydroxide or ammonia. This time, the colour changes to Persian blue. Now add a sodium hydroxide solution gradually to the yellow acidic solution. As soon as the acid is neutralised, the colour changes abruptly to Persian blue. Cochineal carmine may therefore also be used as a pH indicator.

Phenolphthalein — An alcoholic solution of phenolphthalein is one of the most widely used indicators in the laboratory. Since phenolphthalein can be relatively expensive, I generally recommend purchasing a prepared alcoholic solution. A bottle will last a very long time when only a few drops are required from time to time. Alternatively, dissolve 0.5 g of phenolphthalein in 1.5 litres of denatured ethyl alcohol.
A little-known but highly instructive experiment may be performed with this indicator. If carbonic acid solution (sparkling water) is poured into an alkaline solution coloured with phenolphthalein, the pink colour gradually disappears as neutralisation proceeds.

Methyl Orange — Another very common indicator. Unlike phenolphthalein, it may be used in aqueous solution, which can be prepared by dissolving 0.3 g of methyl orange in one litre of hot water.

Bromothymol Blue — This indicator derives its name from the blue colour it exhibits in alkaline media. The following preparation yields a red solution: dissolve 0.2 g of bromothymol blue in 100 mL of 95% ethanol, add 400 mL of water, then heat the mixture to 45–50 °C before bottling.

Readers will find numerous charts on the internet showing the transition ranges of many different indicators. Such charts may be printed and displayed in the laboratory, or even attached directly to the bottles containing the corresponding indicator solutions.

3.2 Specific Reagents

Other substances, more properly described as reagents, make it possible to identify a particular substance or one of its constituents through the colour of the solution or the precipitate produced when the two are brought together. For example, silver nitrate in aqueous solution may be regarded as the reagent for chlorides because, when added to a chloride solution, it produces a white precipitate that rapidly darkens in light, passing through blue and violet shades and sometimes eventually becoming black, depending on the concentrations involved.

The following examples illustrate a number of useful specific reagents.

Reagent for Ammonia and Ammonium Salts (Nessler's Reagent)

To prepare approximately 300 ml of this reagent, proceed as follows... Prepare separately 3.4 g of mercuric chloride ($HgCl_2$) and 9 g of potassium iodide (KI). Prepare about 100 mL of a sodium hydroxide solution having a specific gravity of 1.33. Place the mercuric chloride and potassium iodide in a well-stoppered 100 mL graduated cylinder and gradually add water until the volume reaches 100 mL. At first, the liquid turns yellow and a brick-red precipitate forms. This precipitate gradually dissolves, leaving a golden-yellow solution. Transfer the liquid to a PVC bottle and add a further 150 mL of water, bringing the total volume to approximately 250 ml. Finally, add 75 mL of the sodium hydroxide solution. Leave the bottle standing, without fully tightening the cap during the first few days. With time, the reagent invariably deposits a reddish sediment. When stored in a PVC bottle, it tends to discolor the plastic but causes no other inconvenience.
This reagent produces a readily identifiable precipitate when added to a solution containing an ammonium salt.

Reagent for Chlorine and Bromine

Mix either: 1 mL of aniline with 40 mL of water, or 8 g of phenol, 1 mL of aniline, and

200 mL of water heated to 60–70 °C.
Both reagents should be stored in amber bottles, and the first should be freshly mixed before use. They behave in essentially the same manner. Bromine produces a white precipitate, whereas chlorine produces a reddish-brown precipitate.
Unfortunatelly, despite proper storage precautions, neither reagent can be stored for long periods.

Reagent for Ferric Salts

Sodium thiocyanate, readily available from chemical suppliers, is an excellent reagent for ferric salts. A few drops added to a ferric chloride solution produce a ruby-red colour.
Addition of ammonia to this solution yields a red precipitate of iron thiocyanate.
Addition of nitric acid followed by gentle warming changes the liquid to a golden colour.

Reagent for Calcium Salts

Ammonium oxalate is an excellent reagent for calcium salts and may easily be prepared in solution.
Begin by preparing a solution of oxalic acid. Divide it into two portions, one containing approximately 95% of the total volume and the other the remaining 5%. Neutralise the larger portion with ammonia until the solution reaches approximately pH 7. Then add the remaining unneutralised portion so that the final solution remains slightly acidic. The reagent is then ready for use. When added to a solution containing calcium ions, it produces a white precipitate.

Reagent for Magnesium Salts

Place 2 cm of iodine dissolved in water containing KI in the bottom of a long test tube. Carefully pour limewater on top while stirring. The liquid gradually loses its color and becomes pale yellow. A kind of calcium iodide solution is thus obtained. When this solution is added drop by drop to a solution of a magnesium salt, a brown precipitate forms.

Reagent for Phosphates

Ammonium molybdate is often mentioned as a reagent for phosphates, but it is relatively expensive and, in my opinion, not particularly convenient to use. Magnesia mixture, on the other hand, is remarkably effective and very inexpensive. It may be prepared in either of the following ways:

Method 1

Dissolve 16 g of magnesium chloride and 20 g of ammonium chloride in 160 ml of water. Then add 80 mL of concentrated ammonia solution.

Method 2

Mix 15 g of ammonium chloride with 13 g of magnesium chloride. Add 200 mL of water and a few drops of ammonia so that the final solution is alkaline.

Magnesia mixture produces a heavy white precipitate of ammonium magnesium phosphate when added to a phosphate solution. A similar precipitate may also be produced by orthoarsenates. However, orthoarsenates give a red precipitate with silver nitrate, whereas phosphates produce a white one. Both tests should therefore be performed successively whenever certainty is required.

It is also useful to know that alkaline phosphates produce a white precipitate with aqueous barium chloride.

Reagent for Carbonates

A few drops of hydrochloric acid produce a vigorous evolution of carbon dioxide, particularly when applied to a solid carbonate.

Reagent for Nitrates and Nitrites

Dissolve 3 g of phenol in 20 ml of concentrated sulfuric acid.

Reagent for Alkali Formates and Formic Acid

In a bottle, mix 20–25 mL of concentrated nitric acid with two or three drops of a concentrated solution of potassium or sodium dichromate.
If a few drops of formic acid or a small spatulaful of an alkali formate are added and the mixture is shaken, the colour gradually changes over several minutes from orange to blue owing to the formation of a chromium nitrate.
Neither formates nor formic acid derivatives are known to be mimicked by common substances under these conditions, making the reaction highly characteristic.

Reagent for Aldehydes

Prepare a neutral aqueous solution of fuchsin whose colour ranges from pale pink to deep magenta. Decolourise it completely by adding sulfurous acid drop by drop.

Once decolourisation is complete, an aldehyde such as formaldehyde restores a magenta to violet colour.
This is the well-known Schiff reagent, named after Hugo Schiff (1834–1915).

Reagent for Glucose (Fehling's Solution)

Well known to both chemists and biologists, the reagent developed by Hermann von Fehling (1812–1885) is relatively easy to prepare, despite being sold at a high price by some specialist suppliers.
In bottle A, dissolve 7 g of copper sulfate in 100 mL of distilled water. In bottle B, dissolve 10 g of sodium hydroxide and 6 g of potassium sodium tartrate (Rochelle salt) in 100 mL of water. The two solutions must be stored separately until required, preferably in PVC bottles, since the alkaline solution may eventually attack glass.
Immediately before use, mix equal volumes of the two solutions. When heated in the presence of glucose, the reagent produces a characteristic red precipitate.

Some authors have proposed formulations that do not require storage in separate bottles. One example is as follows:
Dissolve 50 g of tartaric acid and 40 g of sodium carbonate in 300 mL of water and bring the mixture to the boil. Add 50 g of copper sulfate and 40 g of potassium hydroxide. Boil again, then dilute with water to a final volume of one litre.

Reagent for Iodine

Starch paste is the reagent par excellence for iodine. It is prepared by heating distilled water containing dispersed starch. The liquid is then filtered and allowed to cool. Since starch paste has a very limited shelf life, it should ideally be prepared no more than twenty-four hours before use.
In the presence of iodine, it develops a violet to nearly black coloration depending on the amount present. This colour disappears upon heating and reappears when the solution cools.

Differentiating Sulfates from Sulfites

Barium chloride solution is the traditional reagent for sulfates. Unfortunately, it produces a similar white precipitate with sulfites. But the distinction is easily made by adding a small quantity of hydrochloric acid to the precipitate. If the precipitate dissolves, the original substance was a sulfite. If it remains unchanged, the original solution contained a sulfate.

3.3 Polyvalent Reagents

Other reagents are less specific than those described above because they can be used to identify a variety of different substances or constituents. This versatility is often extremely useful in practice. The following examples illustrate a few such reagents.

Formaldehyde + H_2SO_4

Add 0.5 mL of formaldehyde solution to 25 mL of concentrated sulfuric acid.
Two drops of this reagent produce red and white streaks when brought into contact with a phenol.
But the same reagent can also be used to detect:
- Resorcinol (at room temperature, it produces a beautiful cherry-red solution)
- Thymol (when heated, it produces a lilac to red solution)
- Salicylic acid (when heated, it produces a yellow to red solution).

Sodium Hypobromite

This salt has several applications, including its use as a sensitive reagent for urea, ammonia, hydrogen peroxide, and aniline. Its preparation is described in Chapter 5.

Dry Turmeric Paper

In practice, the active colouring principle of turmeric is extracted with alcohol. The resulting solution is then used to impregnate filter paper, which is subsequently dried. The reactions described below occur only with the dry paper and not with turmeric in alcoholic solution.
- Dry turmeric paper turns brown when brought into contact with alkaline solutions. When exposed to ammonia solution (NH_4OH), it also becomes brown, but gradually returns to yellow as the ammonia dissipates. If a drop of sodium hydroxide solution is placed on the still-brown paper, the brown spot turns blue. The same effect is obtained with a drop of ammonia solution that is allowed to dry or evaporate.
- If a few drops of an alcoholic solution of boric acid are placed on dry turmeric paper and allowed to dry, a red coloration appears. Under the same conditions, ferric chloride produces a reddish-brown colour.
Please note that despite proper storage precautions, dry turmeric paper cannot be stored for extended periods.

Logwood Infusion

This coloured reagent provides valuable information concerning the metallic

constituents of a wide variety of salts. Although largely forgotten today in amateur and school laboratories, it remains remarkably useful.
Heat small pieces of logwood in distilled water for approximately ten minutes. Decant the coloured liquid and cool it rapidly. Then add a volume of alcohol equal to one and a half times that of the coloured aqueous extract obtained. Store the reagent in an amber bottle. The active constituent of this preparation is hematoxylin...
Examples:
Potassium → lilac coloration.
Mercury(II) → golden-yellow coloration.
Cobalt → orange coloration.
Nickel → orange coloration.
Copper → black coloration.
Tin → reddish-lilac coloration.
Cadmium → indigo-blue coloration.
Zinc → orange coloration.
Alkali chromate → brown to black coloration, depending on concentration

Several additional reactions deserve mention when the alcoholic hematoxylin solution is diluted with water:
Ammonia (but not ammonium salts) → magnificent purple-red coloration.
Hydrochloric acid → red coloration.
Dilute sulfuric acid → orange coloration that becomes progressively yellower as more water is added.
Nitric acid → gradual decomposition of the colouring matter. When the alcoholic solution is used, the reaction may accelerate markedly, producing nitrogen dioxide. In such cases, fuming nitric acid should never be used, as the reaction may become hazardous.
Baryta water → a precipitate that eventually turns violet on exposure to air. If both solutions have been deprived of dissolved air by prior boiling, the precipitate is initially white and rapidly becomes blue.
Limewater, or any calcium-rich water → mauve coloration.
Lead acetate → blue precipitate. If the solutions have previously been deprived of dissolved air by boiling, the precipitate is white at first.

If a hematoxylin solution in alcohol is diluted with water and ether is then added, the ether layer floating above gradually acquires a yellow colour.

Potassium Ferrocyanide

An aqueous solution of potassium ferrocyanide produces coloured precipitates with various metallic salts. Examples include:
White precipitates: lead, tin, zinc, copper(II), cadmium, antimony.
White gelatinous precipitate: mercury.

White precipitate becoming pink: manganese.
Apple-green precipitate: nickel.
Chlorophyll-green precipitate: cobalt.
Grey-green precipitate: chromium.
Dark green precipitate: molybdenum.
Dark blue precipitate: iron(III).
Reddish-brown precipitate: copper(I).

(Pyro)Gallic Acid

Solutions of gallic or pyrogallic acid produce several characteristic precipitates that permit the easy identification of certain salts:
With ferrous sulfate → blue precipitate.
With ferric chloride → ruby-red or reddish-brown precipitate.
With sodium cyanide → the solution turns red and then gradually fades. Agitation restores the red colour.

Ammonium Thiocarbonate

The attractive yellow crystals of ammonium thiocarbonate do not keep well in air, nor does their aqueous solution remain stable for long. The crystals should therefore be prepared as described in Chapter 5, stored under ether, and dissolved in water only immediately before use. It should also be noted that even when stored under ether, the crystals can be preserved for only a few weeks.
With metallic salts, the aqueous solution of ammonium thiocarbonate produces numerous characteristic reactions, although the exact appearance may vary considerably according to concentration.
Silver salts → yellow precipitate rapidly becoming brown and then grey.
Cobalt salts → pink, red, or black precipitate depending on concentration.
Copper(II) salts → greenish-brown precipitate.
Iron(II) or iron(III) salts → fine ink-black precipitate.
Manganese salts → yellow to green coloration.
Mercury(II) salts → off-white granular precipitate, sometimes tinged with yellow.
Nickel salts → green precipitate.
Lead salts → yellowish-brown to reddish precipitate.
Zinc salts → very fine white precipitate.
Magnesium or chromium salts → no reaction.

Sodium Thiosulfate (Hyposulfite)

An aqueous solution of sodium thiosulfate (historically known as sodium hyposulfite) gives rise to numerous reactions that may be useful in identifying certain mineral salts.

With copper sulfate: the blue solution turns green and rapidly blackens upon heating.
With manganese chloride: no reaction in the cold, but slight cloudiness appears upon heating.
With lead acetate: white precipitate that slowly blackens, even when heated.
With mercuric chloride: white-yellow precipitate that rapidly blackens when heated.
With ferric chloride: precipitate appearing black by reflection but red by transmitted light; upon heating it becomes dirty yellow and eventually deposits a red solid.
With antimony sulfate in sulfuric acid solution: the liquid becomes milky and yellowish after a short time, sometimes requiring gentle heating; stronger heating produces a red-orange colour together with black particles.
With antimony trichloride in hydrochloric acid solution: no reaction in the cold, but heating causes turbidity and sulfur deposition.
With cobalt chloride: no reaction in the cold, but heating darkens the colour and releases a sulfurous odour.
With nickel sulfate: no reaction in the cold, but heating lightens the solution and produces black traces of sulfide.

Ammonium Mercuric Thiocyanate Reagent

Prepare this reagent by dissolving 3 g of mercuric chloride and 3.5 g of ammonium thiocyanate in 100 mL of water.
With a zinc salt, the solution forms a white precipitate of zinc mercuric thiocyanate.
With a zinc salt containing a trace of cobalt, a beautiful blue precipitate is obtained.
With a zinc salt containing a trace of copper, a green precipitate forms while a brown coloration remains above it.
With a cobalt salt, a blue precipitate of cobalt mercuric thiocyanate forms gradually.

Resorcinol Reagent

This little-known method for identifying zinc, nickel, and cadmium ions was first reported in June 1909 in the *Annales de Chimie Analytique* and appears to work particularly well with cadmium ions. Curiously, the author who described the procedure did not mention that it also allows the identification of copper(II) ions.
The method is simple. Ammonia is added slowly to the solution containing the metal salt until any precipitate formed redissolves in an excess of reagent. A solution of resorcinol in alcohol is then added. Within approximately fifteen minutes, the solution changes first to green and then to blue. The colour change occurs more slowly when a solution of resorcinol in ether is used.

The reactions described above already provide the amateur chemist with a substantial collection of attractive, simple experiments that can be performed safely and with very modest equipment.

Chapter 4 - Preparation and Use of Gases

4.1 Continuous Gas Generators

Many devices designed to produce various gases instantly and on demand have been described in the chemical literature. They are generally known as continuous gas generators. All operate according to the same very simple principle: when the stopcock through which the gas leaves the apparatus is closed, the pressure generated inside by the continuing evolution of gas forces away a liquid that was previously in contact with a solid reagent, causing the gas-producing reaction to stop. As soon as the stopcock is reopened, the reaction immediately resumes.

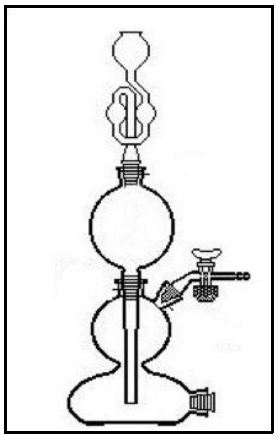


Figure 49

The best-known apparatus of this type is the generator developed in several stages by the pharmacist Kipp (1808–1864), whose name it still bears (Figure 49). In its most perfected form, it consists of three glass bulbs arranged vertically. The upper bulb is connected to the lower bulb by a long tube passing through the central bulb. The solid reagent is placed in this central chamber. When the stopcock connected to the central bulb is opened, the escaping gas allows liquid to rise into that chamber and come into contact with the solid. Fresh gas is then produced, and its flow can be regulated continuously by adjusting the opening of the stopcock. When the stopcock is closed again, the pressure created in the central bulb by the gas still being generated forces the liquid back into the lower bulb and from there into the upper bulb, bringing the reaction to a fairly rapid halt. The apparatus is generally fitted with a safety tube whose main purpose is to isolate the liquid from atmospheric air and to indicate whether pressure or partial vacuum exists within the apparatus as a result of gas production or fluctuations in ambient temperature.

The imagination of chemists seems to have known no bounds when it came to devising apparatus capable of producing gases quickly and conveniently, as the Kipp

generator does. Numerous alternative designs were therefore proposed. The chemist Chaplet described two such devices (Figure 50), both based on the same principles as the Kipp apparatus.

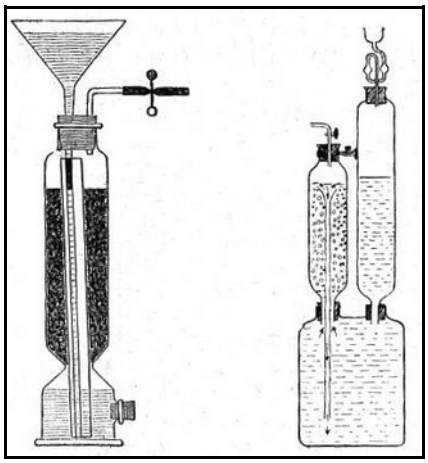


Figure 50

The design shown on the left, however, suffers from a serious drawback: a funnel open to the atmosphere is hardly ideal. Replacing it with a cylindrical funnel fitted with a safety tube would solve one problem but create another, since the apparatus, already somewhat unstable, would become even less so. The apparatus shown on the right, constructed from an ordinary Woulff bottle, is considerably more ingenious and remarkably stable.

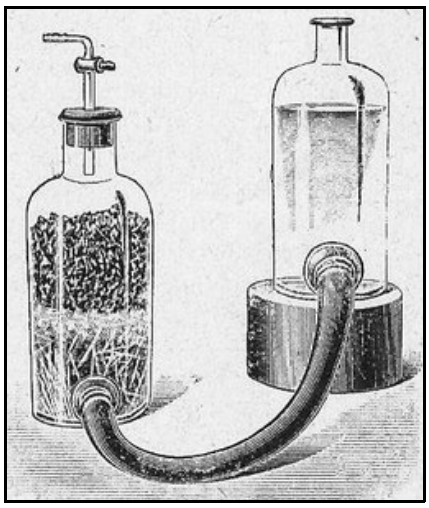


Figure 51

An even better design exists, however, owing to its simplicity. Its invention has been attributed to the chemist Henri Sainte-Claire Deville (1818–1881). It consists of two Woulff-type separating vessels connected by flexible tubing and arranged so that the vessel containing the solid reagent—resting on a layer of broken glass or fragments of earthenware—is positioned slightly below the vessel containing the liquid (Figure 51). The vessel containing the solid is closed by a stopper through which passes a stopcock tube. When the stopcock is opened, part of the liquid from the upper vessel rises into the lower one according to the principle of communicating vessels, and the reaction between liquid and solid begins. When the stopcock is closed, the pressure of the gas formed in the lower vessel drives the liquid back into the upper one. The operating principle is therefore very similar to that of the Kipp generator, but at a much lower manufacturing cost.

An additional advantage is that very large quantities of gas can be produced if required, since vessels of this type are available in capacities of up to 25 liters, whereas even a large Kipp generator rarely holds more than about 5 liters of liquid reagent. In the absence of vessels identical to those used by Deville, a similar continuous gas generator can also be constructed using two tubes or bulbs mounted at different heights on a laboratory stand or even on wall brackets.

The *Encyclopédie chimique* of Frémy and his collaborators reports that the chemist Jean-Jacques Théophile Schloesing (1824–1919) once used an apparatus based on this principle for the production of chlorine. The reaction vessel was immersed in a bath of very hot water, and the solid reagent consisted of compressed pellets of manganese dioxide. Needless to say, such an arrangement was hardly convenient for

routine or repeated use.

One final and rather simple arrangement deserves mention. A large test tube, open tube, or similar container, drilled with a hole at its base, is fixed inside a tall flask with a fairly wide neck (Figure 52). The solid reagent is placed inside this tube, which is then closed with a stopper carrying a stopcock. Once again, opening the stopcock allows the liquid contained in the main vessel to rise into the tube, while closing it forces the liquid back out. If the tube is held in place by a stopper, an additional opening must obviously be provided in that stopper to allow pressure equalization with the atmosphere as pressure changes occur inside the main vessel. As a general rule, the broader the base of the flask, the more stable the apparatus will be. Dare I say that, as a teenager, I had designed the very same apparatus in my small laboratory without ever having seen it described anywhere?

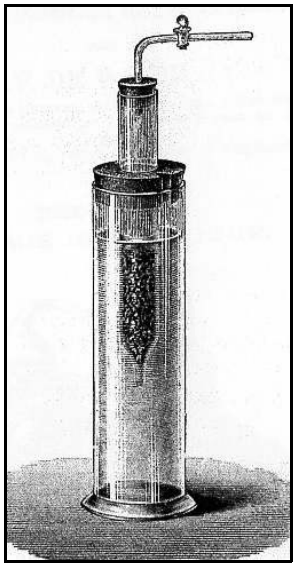


Figure 52

It is remarkable that although several extremely simple and perfectly effective designs could be conceived with only a little thought, some chemists nevertheless invented much more complicated apparatus to accomplish the same purpose. Such was the case with the chemist Brugnatelli (1761–1818), whose apparatus (Figure 53, left) initially impressed the distinguished chemist Carl Remigius Fresenius (1818–1897). The latter eventually judged it so impractical that he substantially modified the design himself (Figure 53, right). Why make things simple when they can be made complicated?

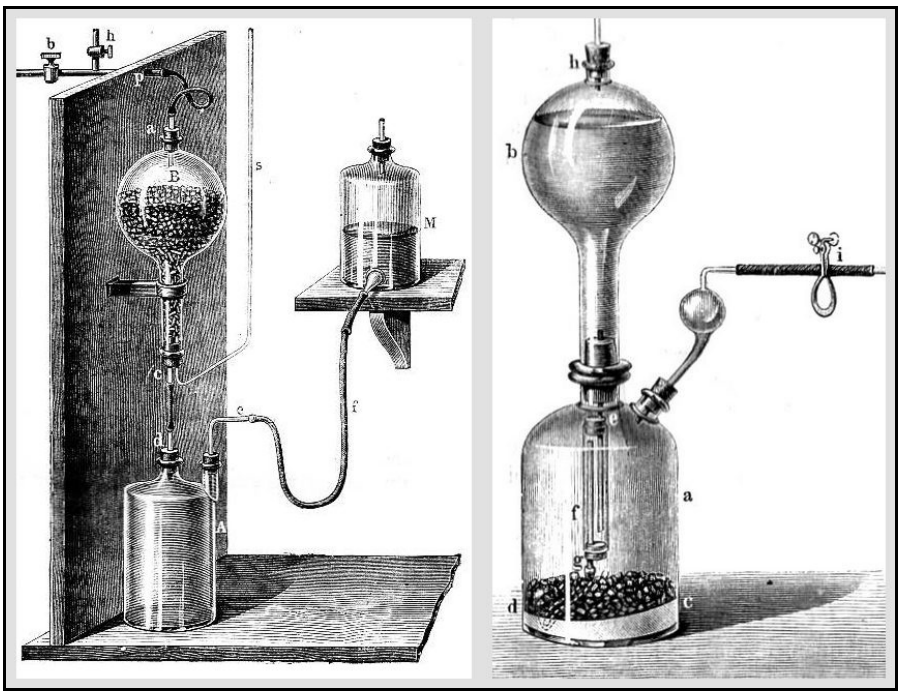


Figure 53

The effective devices described above can function only when the solid reagent remains in large pieces and does not disintegrate into fragments or powder. In ordinary laboratory practice, only four gases can therefore be conveniently prepared using continuous generators: hydrogen (H_2), hydrogen sulfide (H_2S), carbon dioxide (CO_2), and nitric oxide (NO). Even then, a nitric oxide generator must be constructed entirely of glass, without rubber components near the stopcock, because nitric acid and nitric oxide eventually attack rubber and may therefore cause leaks.

Acetylene cannot be produced in a Kipp generator or similar apparatus because calcium carbide does not remain stable in a moist atmosphere. Hydrogen chloride could theoretically be produced using large pieces of salt obtained from a livestock salt block, but practical experience shows (see Section 4.2) that the reaction between concentrated sulfuric acid and sodium chloride does not remain effective for long and works properly only when the salt is already slightly immersed in hydrochloric acid solution. Such a condition would be difficult or impossible to achieve in a Kipp generator. Indeed, if one attempted to prepare a sulfuric acid mixture already containing dissolved hydrochloric acid, hydrogen chloride gas would immediately be liberated.

One might also imagine constructing an all-glass chlorine generator based on the reaction of hydrochloric acid with sodium dichloroisocyanurate tablets. Several objections arise, however. First, the tablets would eventually fragment and disintegrate, falling into the lower chamber.

A device was once proposed for adapting the Kipp principle to reactions in which gas formation results from the interaction of two liquids. It deserves to be described—and criticized—because of both its originality and the rarity with which it appears in the chemical literature.

The inventor suggested that it could be used, for example, to generate gaseous hydrogen chloride from concentrated hydrochloric acid and concentrated sulfuric acid. In this apparatus (Figure 54), the central bulb contained only pumice stone, glass rings, or fragments of porcelain acting as inert packing material. The two remaining bulbs contained concentrated hydrochloric acid.

The Kipp generator was modified by the addition of a stopcock funnel extending deeply into the central bulb through the opening normally occupied by the gas outlet stopcock. When the funnel stopcock (h1) was opened, sulfuric acid flowed over the pumice moistened with hydrochloric acid, producing hydrogen chloride gas that escaped through stopcock h2As soon as stopcock h2 was closed—preferably simultaneously with, or shortly after, h1—the gas still being generated forced hydrochloric acid back into the upper bulb, which therefore could not be filled too completely at the outset.

An additional component completed the system. This consisted of a bulb designated

E, attached to the stopcock funnel and shown in greater detail in a secondary diagram. It was filled with mercury. If the pressure in the central bulb became excessive relative to the gas flow leaving the apparatus, the mercury rose into the funnel tube and acted as a kind of automatic safety valve.

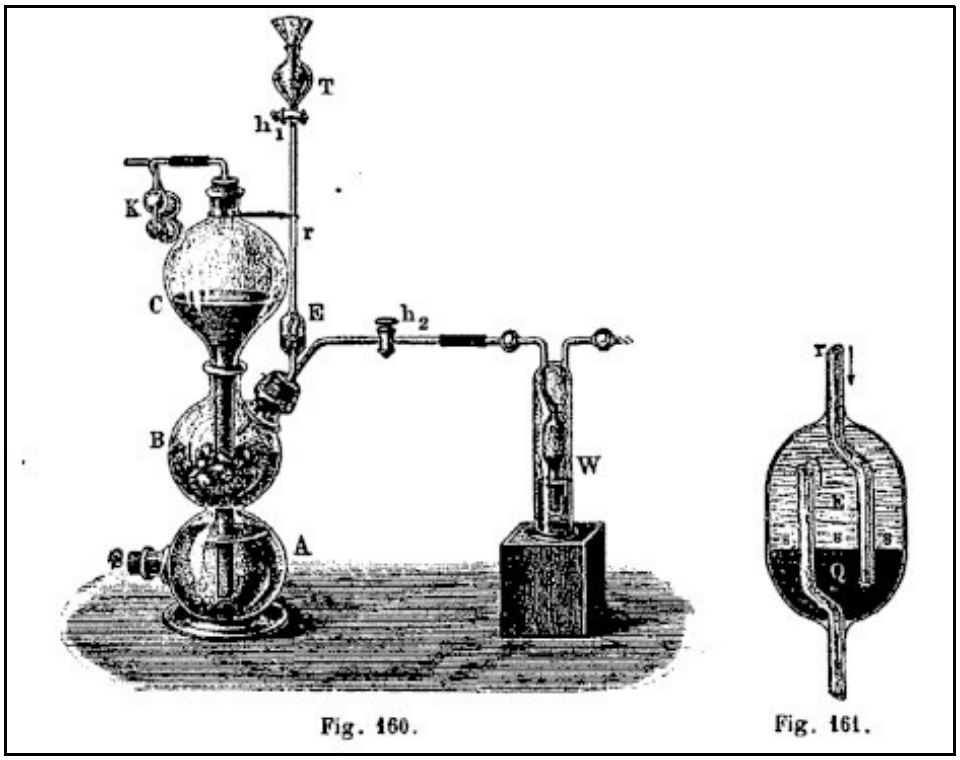


Figure 54

Apart from the fact that this arrangement is astonishingly complicated compared with the very simple apparatus normally required for generating hydrogen chloride gas (see Section 4.2), it also appears largely theoretical. Its inventor seems never to have considered the necessity of preventing prolonged contact between the two acids and atmospheric air. Sulfuric acid would gradually absorb moisture from the atmosphere, while hydrochloric acid would slowly lose hydrogen chloride gas, which would then attack nearby equipment in the laboratory. The apparatus therefore appears less like a practical piece of equipment than the product of a somewhat dreamy—or perhaps eccentric—chemist's imagination.

I should add that professional laboratories no longer use Kipp generators or similar devices. Instead, they rely almost exclusively on compressed gas cylinders. Since this book is intended primarily for amateur chemists, however, the Kipp generator and related apparatus certainly deserve mention.

The time has now come to examine the various reactions that can be used to prepare most of the gases commonly employed in chemical experiments.

The overwhelming majority of authors have traditionally described—and continue to describe—more or less the same methods of gas preparation. Yet these methods

are not always the most appropriate, nor are they necessarily the least expensive. Oxylyth, for example, which was long used for oxygen production despite its hazardous storage properties, is now sold at extremely high prices. With a little ingenuity, however, oxygen can be prepared from very inexpensive materials.

But let us examine the matter more closely...

4.2 Methods for Preparing Gases

IMPORTANT NOTE

We are now entering the truly experimental part of this book. Readers will therefore understand why the style occasionally becomes less literary and more directly focused on the practical description of chemical procedures.

OXYGEN — O_2

1) Allow a solution of potassium permanganate ($KMnO_4$) acidified with sulfuric acid (H_2SO_4) to flow onto sodium perborate. This is by far the least expensive and easiest method for preparing oxygen in the laboratory.
NOTE: Once a significant quantity of liquid has accumulated in the reaction flask, it is useful to employ a magnetic stirrer in order to obtain a complete and steady evolution of gas. This observation also applies to several other gas preparations.

2) Allow a hot solution of sodium perborate to flow onto manganese dioxide (MnO_2). This is also an effective method for preparing oxygen.

3) Allow a hot solution of sodium perborate to flow into an aqueous solution of manganese sulfate or manganese chloride. This more costly procedure is primarily a laboratory curiosity.

4) Add hydrogen peroxide dropwise onto solid potassium permanganate (or potassium permanganate moistened with only a very small quantity of water), or onto lead dioxide (PbO_2) covered by a very shallow layer of water. Since each drop produces a kind of miniature explosion, this method is effective but poorly suited to obtaining a regular evolution of gas.

5) Add hydrogen peroxide (H_2O_2) dropwise to a solution of potassium permanganate acidified with sulfuric acid.

6) Add hydrogen peroxide acidified with hydrochloric acid or sulfuric acid dropwise

onto manganese dioxide. Here again, each drop triggers a miniature explosion.

7) Add hydrogen peroxide dropwise to bleach solution or chlorine water.

8) A simple, original, and little-known method for producing oxygen steadily consists of placing a piece of gold foil in a flask containing a small quantity of hydrogen peroxide. Gentle heating initiates the reaction, after which oxygen is evolved continuously without further heating. The gold remains completely unchanged and can therefore be reused many times. Finely divided gold powder should not be used, however, since the reaction may then become explosive.
NOTE: The reaction of hydrogen peroxide with certain metals can be quite surprising. At ordinary temperature, zinc already causes the evolution of oxygen. When heated, oxygen is evolved in the presence of iron, copper, tin, aluminum, silver, and gold. The effect is least pronounced with aluminum. The experiment can naturally be extended to other metals. Powdered metals often react even at room temperature, as do certain powders, oxides, and mineral salts. A great many experiments may therefore be performed. In many cases the metals act merely as catalysts and remain chemically unchanged.

Hydrogen peroxide generally evolves oxygen, but not always. For example, when it reacts with carbon, carbon dioxide is produced instead. Descriptions of numerous reactions between hydrogen peroxide and a wide variety of substances—either alone or mixed together—may be found in: MELLOR, J. W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London, Longmans Green and Co., 1922, Vol. I, pp. 936–946.

WARNING: Reactions involving the decomposition of hydrogen peroxide may be extremely violent. They should always be carried out cautiously and, when testing reactions with powders or unfamiliar substances, only with very small quantities of liquid.

9) Heat a mixture of sulfuric acid diluted with half its volume of water and powdered manganese dioxide. The manganese sulfate produced may subsequently be recovered.

DILUTION OF SULFURIC ACID IN WATER

WARNING! It is worth emphasizing that water and sulfuric acid must always be mixed by slowly pouring the acid into the water, while stirring continuously and monitoring the temperature. The reverse procedure may cause dangerous acid splashes and severe burns.

10) Heat an intimate mixture of potassium chlorate and previously ignited

manganese dioxide. The manganese dioxide should first be calcined in order to destroy any organic matter that may be present and could otherwise cause a violent runaway reaction. For the same reason, cork stoppers should not be used. Because of the hazards associated with this once-classical preparation, it should now be regarded only as a laboratory curiosity and carried out, if at all, with very small quantities of reagents.

11) Heat potassium dichromate with an excess of sulfuric acid. The mixture foams and turns green owing to the formation of chromium sulfate, $Cr_2(SO_4)_3$. The gas evolved is oxygen, but the yield is poor and the cost excessive. Moreover, dichromate compounds are carcinogenic and should be handled as little as possible in large quantities. This method should therefore remain nothing more than a laboratory curiosity.

12) Prepare a 30% aqueous solution of sodium hydroxide and add a few drops of a concentrated cobalt salt solution. Heat to approximately 30 °C and remove the source of heat. A moderate stream of chlorine gas is then introduced. The precipitated cobalt compound darkens, becoming black. Effervescence follows, accompanied by a rise in temperature and the evolution of oxygen. This is again more of a laboratory curiosity than a practical or safe method for producing oxygen.

13) Heat bleach solution almost to boiling and slowly add a solution of nickel sulfate. A black precipitate forms, while the liquid foams vigorously and evolves oxygen. Care must be taken to avoid a runaway reaction. The evolution of oxygen will be weak and scarcely noticeable unless the nickel sulfate solution is fairly concentrated. This is therefore an expensive process that I do not recommend for regular use.

14) Heat bleach solution containing a knife-tip quantity of cobalt chloride crystals. As the darkened liquid is heated gently, it eventually begins to foam vigorously and evolve oxygen. This procedure is little more than a laboratory curiosity, since large quantities of water vapour are rapidly produced as the temperature approaches or reaches the boiling point.

IMPORTANT NOTE: Oxygen should always be dried with sulfuric acid, calcium chloride, or sodium hydroxide, and washed with water.

OZONE — O_3

Ozone is one of the gases that an amateur chemist can least easily produce in reasonable quantities, since its preparation generally requires sophisticated electrical equipment.

There is, however, a simple method for producing a very small amount of it—sufficient nevertheless to perceive its characteristic odour.

In a small dish, mix equal parts of potassium permanganate ($KMnO_4$) and barium peroxide (BaO_2) thoroughly together. Once this has been done, add a few drops of sulfuric acid. Purple fumes, which should not be inhaled, are evolved, and at the same time an odour reminiscent of the seashore may be perceived. This is the characteristic smell of ozone, which may also sometimes be noticed after a thunderstorm.

HYDROGEN — H_2

1) React dilute hydrochloric acid with zinc or iron. This is by far the most practical and least expensive method.
NOTE: If the zinc is too pure, the reaction may fail to start. In such cases, simply touching the zinc with a platinum or copper wire, or adding a few drops of copper sulfate solution, will create a galvanic couple and initiate the reaction.

2) React dilute sulfuric acid with zinc or iron. In practice, however, this method is not recommended for the continuous production of large quantities of hydrogen. Zinc sulfate is far less soluble than zinc chloride and therefore tends to deposit on the surface of the metal, gradually forming a barrier that hinders the action of the acid.

3) React moderately diluted hydrochloric acid with aluminum. Since the reaction tends to accelerate uncontrollably, it is poorly suited to obtaining a regular evolution of gas and should be regarded merely as a laboratory curiosity.

4) React concentrated sodium hydroxide solution with aluminum. This reaction produces considerable heat and likewise tends to run away. It is therefore not recommended because of its irregular behaviour.

5) Heat 20 g of zinc filings mixed with a few grams of iron in a 10% sodium hydroxide solution until gentle boiling is reached. The hydrogen obtained is purer than that produced by the preceding methods, but the gas is heavily laden with water vapour, which must be removed by means of a cold trap. Consequently, this method also remains largely a laboratory curiosity, at least for amateur chemists and many schools.

6) Place three compressed balls of aluminum foil, each approximately 1 cm^3 in volume, in a test tube. Add a small spatula-tip quantity of mercuric chloride and some water. Hydrogen evolution begins gradually and then accelerates. An amalgam is formed, mercury is released, and the water is decomposed until the aluminum has been completely oxidized. This is obviously nothing more than a costly and entirely unnecessary laboratory curiosity for the preparation of hydrogen.

IMPORTANT NOTE: Hydrogen should always be dried with sulfuric acid, calcium chloride, or quicklime (CaO), and washed with water.

Hydrogen produced from zinc often contains arsenic, sulfur, and phosphorus compounds. The famous chemist Dumas purified it by passing it successively through solutions of lead, mercury, and silver salts, followed by concentrated sulfuric acid, which retained both water vapour and hydrocarbon impurities. In schools and amateur laboratories, such precautions are rarely necessary. If one nevertheless wishes to obtain hydrogen free of arsenic compounds, it is sufficient to pass the gas through two potassium permanganate solutions, one acidic and the other alkaline.

HYDROGEN CHLORIDE OR HYDROCHLORIC ACID — HCl

1) Allow sulfuric acid to flow onto common salt (NaCl). To prevent the formation of a compact crust that the acid can no longer attack, it is preferable to use coarse salt rather than fine salt and to moisten it with hydrochloric acid beforehand. This is by far the best method. In laboratories, the reaction is usually carried out at room temperature. In industry, however, better yields are obtained by heating above 100°C.

2) A closely related process uses ammonium chloride in place of common salt. Since this method is considerably more expensive, it should be regarded either as a laboratory curiosity or as a means of obtaining particularly pure hydrogen chloride.

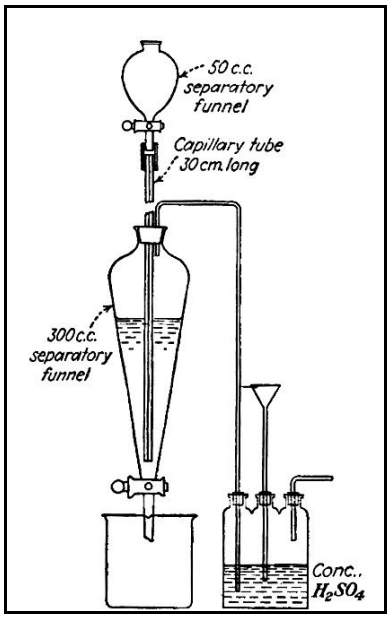


Figure 55

3) Allow sulfuric acid to flow into concentrated hydrochloric acid. Since sulfuric acid does not dissolve hydrogen chloride, the latter is liberated as a gas.

The first volume of the series *Inorganic Syntheses* (edited by Harold Simmons Booth, 1939) describes a continuous generator based on this reaction. The apparatus consists essentially of two stopcock funnels. The upper one, having a capacity of approximately 200 mL and containing sulfuric acid, is connected by a capillary tube to a much larger lower funnel containing hydrochloric acid. The capillary tube passes through a two-hole stopper. The second opening carries a long glass tube leading to a wash bottle containing sulfuric acid. The lower vessel is of the stopcock-funnel type simply because this makes it easier to empty and refill when the hydrochloric acid must be renewed. Fresh acid can then be introduced through the upper funnel after it has first been emptied of sulfuric acid (Figure 55).

It will be noticed, however, that this arrangement differs very little from the classical apparatus in which acid from a dropping funnel is allowed to fall onto salt previously

moistened with hydrochloric acid and placed in a flask.

4) It is sometimes stated that hydrogen chloride can be prepared simply by heating a concentrated aqueous solution of hydrochloric acid. In practice, however, the gas rapidly becomes saturated with water vapour. Removing this moisture requires a relatively complex apparatus including, among other things, a cold trap. This method is therefore not recommended.

IMPORTANT NOTE: Always dry hydrogen chloride gas with concentrated sulfuric acid and never attempt to wash it with water, since it is extremely soluble in that liquid.

CHLORINE — Cl_2

1) Allow hydrochloric acid to fall dropwise onto pieces of sodium dichloroisocyanurate or, better still, onto pieces of trichloroisocyanuric acid.
These two substances have the advantage of being readily available at modest cost because they are now widely used for the treatment of private swimming pools. At present, this is by far the simplest and least expensive method for producing large quantities of chlorine.

2) Allow hydrochloric acid to flow onto solid potassium permanganate.
For many years, this remained the simplest method for obtaining pure chlorine.

3) Heat a mixture of hydrochloric acid and manganese dioxide.
Although the reaction begins at room temperature, heating is subsequently required if it is to continue at a satisfactory rate and provide a good yield. Some authors recommend adding a mixture of sulfuric acid and hydrochloric acid to manganese dioxide. In practice, this offers little advantage.
Certain authors further state that the manganese chloride formed can easily be recovered. This is, however, more attractive in theory than in practice. Manganese dioxide is rarely pure, and a variety of other salts are therefore formed at the same time. To obtain pure manganese chloride, any excess acid would first have to be neutralized with chalk, which would also precipitate ferric oxide. After decantation, ammonium sulfide would then have to be added drop by drop until the precipitate, instead of being black, became pink. This would indicate that only the desired manganese chloride remained in solution and that the liquid could be filtered. It is easy to understand that such operations would only be justified if one wished to recover a large quantity of manganese chloride, a situation that is encountered very rarely.

4) Add hydrochloric acid dropwise to bleach solution while stirring with a magnetic stirrer to promote a steady evolution of gas.
The disadvantage of this method is that it may produce oxygen-containing chlorine compounds in addition to chlorine itself.

5) Add hydrochloric acid dropwise to bleaching powder.
This process, once very widely used, presents several significant disadvantages. First, bleaching powder—now rather misleadingly sold as calcium hypochlorite—is in reality an unstable mixture of basic calcium hypochlorite [$Ca(ClO)_2 \cdot 2Ca(OH)_2$] and basic calcium chloride [$CaCl_2 \cdot Ca(OH)_2$]. Over time, this mixture gradually loses its available chlorine and consequently becomes less and less effective for chlorine production. Furthermore, the chlorine evolved may be contaminated with carbon dioxide because the lime used in the manufacture of bleaching powder often contains calcium carbonate impurities. Finally, this product is now used so infrequently that it has become difficult to obtain material of good quality that has been manufactured recently. Indeed, bleaching powder keeps poorly unless it is stored in perfectly airtight containers.

6) Mix solid potassium dichromate with hydrochloric acid and heat moderately.
The reaction is vigorous and produces considerable foaming. A large flask, preferably of round-bottomed type, should therefore be used to prevent overflow. This is a relatively expensive method and a highly polluting one because of the chromium compounds involved.

7) A few authors recommend adding concentrated sulfuric acid to a mixture of sodium chloride and manganese dioxide.
The reaction is supposed to produce hydrogen chloride, which would immediately react with the manganese dioxide to generate chlorine. In practice, however, this is not what happens. Either hydrogen chloride escapes before it has time to react with the manganese dioxide, or it contaminates the chlorine that is evolved. This procedure should therefore be regarded as nothing more than a laboratory curiosity.

8) Add concentrated hydrochloric acid to potassium chlorate.
The reaction is fairly vigorous. Better control and a steadier evolution of gas can be obtained by first immersing the chlorate in a little water and then adding the concentrated acid to the mixture. Gentle heating may subsequently be used to increase the rate of gas evolution. This method remains a laboratory curiosity because, apart from its cost, the chlorine produced may be contaminated with the highly dangerous gas chlorine dioxide (see below)

9) In the second method described above (hydrochloric acid and potassium permanganate), the permanganate may be replaced by other oxidizing agents such as lead dioxide (PbO_2), red lead (Pb_3O_4), or even chromium trioxide (CrO_3). These alternatives are considerably more expensive and are therefore seldom mentioned in practice. They should be regarded solely as laboratory curiosities.

IMPORTANT NOTES: Always dry chlorine with concentrated sulfuric acid or calcium chloride, and wash it with a small quantity of water.

Chlorine attacks both rubber and silicone. For this reason, whenever substantial

quantities of chlorine are being used, it is strongly recommended that only ground-glass apparatus be employed, or alternatively rubber stoppers whose lower surfaces have first been coated with a protective grease layer.

CHLORINE DIOXIDE — ClO_2

The action of sulfuric acid on potassium chlorate produces chlorine dioxide, a highly toxic gas that explodes upon contact with many substances, whenever its concentration in air exceeds 10%, or when it is heated to approximately 65°C. For this reason, under no circumstances should this gas be prepared except during the limited experiments described later in this book and only by strictly following the precautions indicated there.

As a simple laboratory curiosity, however, sulfuric acid may be added very cautiously, drop by drop, to potassium chlorate. A yellow gas then gradually appears. The mixture must never be heated or brought into contact with any other organic or mineral substance. Once the formation of the gas has been observed, the mixture should be flooded from a safe distance with water from a wash bottle and then poured into a bucket of water for further dilution and final disposal.

The reaction between potassium chlorate and hydrochloric acid, or certain other acids, produces highly oxidizing and dangerous mixtures of chlorine dioxide and chlorine. Such mixtures which were once used to destroy organic matter should never be carried out without adequate knowledge and suitable equipment. As a simple laboratory curiosity, however, a small quantity of powdered potassium chlorate may be mixed with powdered oxalic acid in a test tube, after which two or three drops of water are added.

ClO_2 AND PSEUDOSCIENCE

The internet is now full of nonsense concerning chlorine dioxide. According to some claims, it is a miracle remedy, and its aqueous solution has been marketed under the names *Miracle Mineral Supplement* or *Miracle Mineral Solution*, both commonly abbreviated as MMS. Numerous tutorials—many of them particularly absurd—may be found online, especially on YouTube, explaining how to prepare this supposed miracle solution. In reality, such claims are founded on ignorance. The origin of this dangerous pseudoscience can be traced to a self-published book by the engineer Jim Humble, a member of the Church of Scientology. Several official organizations, including the *Food Standards Agency* and the *Belgian Poison Centre*, have issued severe warnings concerning MMS and its alleged medicinal properties.

BROMINE — Br_2

PRELIMINARY NOTE: Bromine is most often used in its liquid form. Nevertheless, in view of certain of its properties, it is not incorrect to regard it as a gas and to prepare and use it as such.

DANGERS OF BROMINE

Breathing bromine is just as dangerous as breathing chlorine. Bromine can also cause severe skin burns. In the event of skin contact, wash the affected area immediately with water, then pour benzene onto it. This old laboratory remedy converts the bromine into bromobenzene, which is far less corrosive.

Because of the hazards associated with liquid bromine, some laboratories prefer not to store it and instead prepare it as required by one of the methods described below.

1) Prepare a mixture containing equal weights of manganese dioxide (MnO 2) and potassium bromide (KBr). Allow sulfuric acid, either concentrated or only slightly diluted, to flow gradually onto the mixture while applying gentle heat, at least during the initial stages of the reaction. The preparation should be carried out in an apparatus made entirely of glass, preferably immersed in a moderately warm water bath. The bromine vapours are first cooled and condensed before being led into a separatory funnel containing water by means of a delivery tube dipping beneath the liquid surface. The bromine collects beneath the water layer while only a small portion dissolves in it.

The bromine may then be recovered simply by opening the stopcock of the separatory funnel. Care should be taken not to empty the funnel completely. A few millilitres of bromine, together with all of the water originally present, should be transferred to a separate flask. After prolonged contact, these two substances will provide an excellent bromine water solution.

2) Bromine is also evolved if sulfuric acid in the preceding method is replaced by weaker acids. The reaction is, however, much less effective and should therefore be regarded merely as a laboratory curiosity.

3) Bromine is likewise produced when a mixture of potassium bromide and potassium dichromate (or sodium bromide and sodium dichromate) is treated with sulfuric acid.

The reaction foams considerably, and the salts tend to form a compact mass. It is therefore useful to moisten them beforehand and place them in a fairly wide flask before adding the acid dropwise.

NOTE: In this last experiment, replacing the bromide with an iodide results in the evolution of iodine rather than bromine. Recovering the iodine in solid form is, however, somewhat difficult.

HYDROGEN IODIDE OR HYDROIODIC ACID — HI

Of all the gases discussed in this chapter, this is, in my opinion, the most difficult to prepare if one wishes to use it in the gaseous state.

1) Place no more than 5 to 10 mL of water in a flask. Add half a spoonful of red phosphorus and then a quantity of iodine approximately twice as great as that of the phosphorus. The iodine must be present in considerable excess in order to prevent the formation of dangerously unstable phosphorus iodide compounds. According to the chemist Sainte-Claire Deville, a concentrated potassium iodide solution may be used instead of water to improve the regularity of the reaction. Heat the mixture very gradually. Most books recommend trapping the iodine vapours carried over during the reaction in a tube containing broken glass, red phosphorus, and a small quantity of water. I believe, however, that it is both simpler and less expensive to condense these vapours in a cold trap immersed in ice water.

2) In a small flask, heat a mixture of equal parts iodine and concentrated phosphoric acid. At first, iodine vapours are evolved and may be condensed in a cold trap. Hydrogen iodide is then liberated. Because of its poor yield, this method should be regarded only as a laboratory curiosity.

NOTE: Rather than working with gaseous hydrogen iodide, it is generally preferable to prepare an aqueous solution by allowing the gas to enter water through a delivery tube fitted with a safety bulb, with only the tip of the tube immersed. Cooling the water and stirring it with a magnetic stirrer increase the solubility of the gas.

3) Another way of preparing an aqueous solution of hydroiodic acid is to bubble hydrogen sulfide—previously passed through a small quantity of water to remove any hydrochloric acid it may contain—through a U-tube containing water and iodine. The liquid becomes milky, and the colour of the iodine gradually disappears. The mixture is then allowed to stand, filtered, and briefly boiled to expel the hydrogen sulfide dissolved in the water.
The U-tube may subsequently be cleaned with ammonium sulfide, which dissolves the sulfur adhering to the walls (see end of this book).
If, instead of adding iodine directly to the water, a solution of iodine in chloroform is used, the reaction proceeds more readily. In that case, the two liquid layers should be separated by decantation before filtration.

This is the simplest method for preparing an aqueous solution of hydroiodic acid.
If one wishes, for teaching purposes, to show exactly what occurs during the reaction, the experiment may be performed in a more demonstrative manner by

passing hydrogen sulfide through a Drechsel bottle placed on a magnetic stirrer and containing water, starch, iodine, and a very small quantity of potassium iodide. The potassium iodide serves to facilitate the dissolution of iodine in water. The liquid then acquires such a deep violet colour that the bottle appears almost black. When the stream of hydrogen sulfide is started, the dark colour gradually disappears and the liquid slowly becomes yellowish. If the stirrer is then stopped and the liquid allowed to stand, it becomes apparent that the colour was due to finely suspended sulfur (Figure 56).

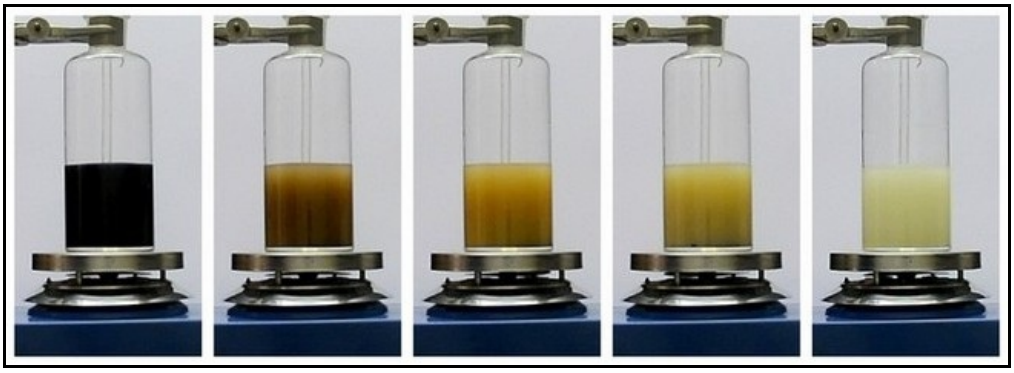


Figure 56

This beautiful experiment is valuable only from a pedagogical standpoint, since it is not possible afterward to separate the hydroiodic acid easily from the other substances present in the bottle.

4) A simple way of preparing an aqueous solution of hydroiodic acid directly is to pass hydrogen sulfide through water containing freshly prepared lead iodide. Black lead sulfide is formed, gradually replacing the original yellow compound. The reaction is therefore easy to observe and to stop at the desired moment. The liquid need only be filtered and then briefly boiled to expel any remaining hydrogen sulfide.

5) In his book *Chemical Lecture Experiments* (New York, Macmillan Company, 1909), the chemist Francis G. Benedict explained that hydroiodic acid could easily be prepared by heating a mixture of equal parts iodine and rosin, to which sand was added in order to moderate the reaction. Although hydroiodic acid is indeed produced in this process, large quantities of iodine vapour and a greasy substance are evolved as well. Rather than employing the purification systems proposed by Benedict, I believe it is preferable to use a simple cold trap immersed in ice water. The loss of iodine is nevertheless considerable, and the entire apparatus must subsequently be cleaned with aceton. This method is therefore best regarded as a laboratory curiosity.
NOTE: Hydrogen iodide is a very dense gas and is collected by displacement, in the same manner as chlorine (see Section 4.3.1). It cannot be collected over mercury, which it attacks, nor over water, in which it dissolves readily. Its solution cannot be stored for more than a few days or weeks, even in a tightly stoppered amber bottle, since iodine gradually separates from the solution during storage. There is therefore

always an advantage in using it as soon after preparation as possible

HYDROGEN BROMIDE OR HYDROBROMIC ACID — HBr

1) Place in a flask a mixture consisting of 1 part red phosphorus and 4 parts sand. Moisten it with a small quantity of warm water. Bromine is then added very slowly, drop by drop, while the reaction is continuously monitored. A small explosion occurs with each drop. The gas is collected after passing through a tube containing moist red phosphorus mixed with Raschig rings. These rings may subsequently be thrown into a little water, after which the liquid floating above them may be recovered as hydrobromic acid solution. The bromine may be replaced by bromine water, used at its maximum concentration (saturated solution), and allowed to fall directly onto the red phosphorus. Since this reaction is highly exothermic, it is advisable to place the reaction flask in an ice-water bath.
This is the best method for preparing hydrogen bromide in the gaseous state.

2) Bromine containing a small quantity of carbon disulfide is allowed to flow gradually onto naphthalene. Gentle heating may be applied if necessary. After the reaction has gone to completion, the residue remaining in the flask may be shaken with sodium hydroxide solution and distilled. Colorless naphthyl bromide is then obtained.
A somewhat different way of carrying out the same operation consists of adding bromine to naphthalene mixed with iron filings while the reaction vessel is maintained in a water bath at approximately 40 °C.
Finally, bromine may be added gradually to naphthalene dissolved in xylene and containing a small quantity of iron powder.

3) Naphthalene may be replaced by the kerosene traditionally used in oil lamps. In this case, the apparatus consists of a flask or Erlenmeyer flask immersed in a water bath maintained at approximately 40 °C. Kerosene is placed in the vessel and stirred magnetically. Bromine is then added dropwise through a dropping funnel. Owing to the agitation, the reaction proceeds smoothly and hydrobromic acid gradually escapes through the outlet tube. It may then be directed into a U-tube containing water cooled by an ice-water bath.
For demonstration purposes, a much simpler experiment may be performed by adding a few drops of bromine to kerosene contained in a test tube and shaking the mixture in the open air. A cloud forms above the mouth of the tube as the acid comes into contact with atmospheric moisture. The strongly acidic nature of this cloud may easily be demonstrated with a moistened indicator paper.

4) Place benzene and iron powder in a flask. Bromine is then added through a dropping funnel. A short outlet tube should immediately lead into a U-tube containing water. The hydrobromic acid evolved dissolves in the water contained in the U-tube. The reaction does not necessarily begin at once. Once it has started, however, vigorous cooling is required to prevent the benzene from distilling over.

Later, the reaction becomes much calmer and it may even be necessary to apply gentle heating by means of a water bath.
Since the experiment is difficult and the yield poor, it should be regarded merely as a laboratory curiosity.

5) Heat solid paraffin wax to approximately 180°C, well below its boiling point, and allow bromine to fall into it. The reaction is vigorous and difficult to control. It should therefore be regarded merely as a laboratory curiosity, especially since the reaction vessel—preferably a simple test tube—is afterward almost impossible to clean.

6) Pass chlorine through bromine and then heat the yellow liquid thus obtained (bromine chloride). Hydrogen chloride is evolved, leaving hydrogen bromide behind. Bromine chloride is soluble in water and may be extracted from it with ether. In the presence of hydrogen peroxide, it produces oxygen.
As the reader will readily understand, this is more of a laboratory curiosity than a rational method for preparing hydrobromic acid.

7) Heat solid potassium bromide in concentrated phosphoric acid. The reaction proceeds quietly over a low flame but gives a very poor yield.

8) Dissolve 51 g of sodium bromide or 60 g of potassium bromide in 200 mL of water. Place the solution in an ice-water bath and slowly add 45 mL of concentrated sulfuric acid while carefully preventing any rise in temperature. The liquid is then distilled using a fractionating column of the Vigreux type, and only the fraction passing over at 125°C is collected. A 48% hydrobromic acid solution is thus obtained. The yield has, however, seemed rather disappointing to me, and I am therefore inclined to regard this method as more of a laboratory curiosity than a practical preparation.

Hydrobromic acid is frequently used as an aqueous solution, which keeps very well in tightly stoppered amber bottles. It may be prepared simply by dissolving the gas directly in previously boiled and cooled water. The simplest arrangement consists of a U-tube partially filled with water and immersed in an ice-water bath.

Another method of obtaining an aqueous solution of hydrobromic acid is to pass hydrogen sulfide through a U-tube containing a mixture of water and bromine. Once all the bromine has disappeared, the liquid is filtered and briefly boiled to expel dissolved hydrogen sulfide. Alternatively, it may be distilled, a 48% hydrobromic acid solution passing over at 125 °C. Although this latter method yields a relatively pure solution, it also involves a substantial overall loss of acid.

NOTE: Hydrogen bromide is heavier than air and therefore easily collected by allowing it to "flow" into a vessel, much as one would do with chlorine or carbon dioxide. It cannot be collected over mercury or over water.

AMMONIA — NH_3

1) Place powdered ammonium chloride in a flask and then add pellets or beads of sodium hydroxide on top of it. Close the flask very quickly and then allow water to enter drop by drop onto the two substances. This very simple procedure is perfectly suitable for obtaining ammonia rapidly, although part of the gas will inevitably dissolve in the water being added.
The same method may also be applied to other ammonium salts, such as the nitrate, oxalate, sulfate, tartrate, phosphate, or hydrogen phosphate. Since these salts are much less common than ammonium chloride, however, their use should be regarded merely as a laboratory curiosity.

2) Allow highly concentrated aqueous ammonia to fall dropwise onto solid sodium hydroxide or potassium hydroxide. Since the reaction is strongly exothermic, it may be useful to immerse the flask in cold water or even in an ice-water bath.

3) Heat concentrated aqueous ammonia containing a few pieces of charcoal and a few drops of sodium hydroxide solution. Although this method is very simple, it often makes it necessary to dry the gas afterward, either by passing it through a column containing quicklime or by using a cold trap.

4) Heat either an intimate mixture of quicklime and ammonium chloride or a thick paste of slaked lime and ammonium chloride.
This procedure is less convenient than the preceding ones because it requires more preparation and may damage the glass reaction vessel.

IMPORTANT NOTE: Ammonia should be dried only with quicklime (CaO) or granular sodium hydroxide, never with calcium chloride, which absorbs ammonia.

Some authors recommend passing the gas through a concentrated caustic potash solution, which is said to dissolve only a small quantity of ammonia while retaining part of the water vapour with which it may be mixed. I mention this method only for the sake of completeness and as an historical curiosity, since it seems highly questionable to me.

HYDROGEN SULFIDE OR HYDROSULFURIC ACID — H_2S

1) React iron sulfide (FeS) with dilute hydrochloric acid (at least one volume of HCl to one volume of water).
When using a Kipp generator, the acid should be well diluted in order to prevent hydrogen chloride, gradually released from the acid during storage, from continuing to react with the iron sulfide and eventually causing the generator to overflow after several weeks. There is, however, nothing to fear if the apparatus is used regularly.
The gas produced by this reaction generally contains a small amount of hydrogen because iron sulfide often still contains traces of metallic iron. In most cases,

however, the hydrogen evolved together with the hydrogen sulfide causes no inconvenience.

2) React finely powdered black antimony sulfide with hydrochloric acid. The reaction begins at room temperature but subsequently requires heating.

3) Some authors recommend reacting iron sulfide with very dilute sulfuric acid (one volume of sulfuric acid to fifteen volumes of water). This procedure is not recommended because compounds are formed that rather quickly slow down the reaction. For this reason, a hydrogen sulfide Kipp generator should not be operated with sulfuric acid.

IMPORTANT NOTE: Always dry hydrogen sulfide with calcium chloride and never with sulfuric acid (see Chapter 9.8 for the reason). Wash the gas only with a small quantity of water, since hydrogen sulfide is soluble in it.

HYDROGEN SELENIDE — H_2Se

In a small porcelain dish, mix powdered aluminium with powdered selenium. The mixture is then heated directly in the flame of a blowtorch or ignited by means of a magnesium ribbon, although the latter procedure is not particularly easy. A small quantity of a yellowish substance is thus obtained. This substance is aluminium selenide. When brought into contact with water, it evolves hydrogen selenide, a gas possessing an unpleasant odour somewhat similar to that of hydrogen sulfide, but considerably stronger.
It is also substantially more toxic than hydrogen sulfide and should therefore be handled with great caution and only outdoors.
Apart from its preparation as a scientific curiosity, this gas has no practical use in an amateur laboratory.

CARBON MONOXIDE — CO

1) Prepare a mixture of 1 part thoroughly dried citric acid and 4 parts concentrated sulfuric acid. Heat gently and intermittently, taking care never to exceed 40 °C, since higher temperatures would lead to the formation of other products, including carbon dioxide and aceton. A considerable evolution of carbon monoxide is obtained, while the liquid acquires a beautiful yellow colour. When this colour begins to turn brown, the experiment should be stopped, as sulfur dioxide and other substances would then begin to be evolved. The odour reveals that acetic acid has been formed in the reaction flask.
As a precaution, the gas should always be washed through limewater in order to prevent contamination by carbon dioxide.
This method is extremely practical and inexpensive.

2) Place sodium formate or potassium formate in a flask and gradually add concentrated sulfuric acid. The reaction begins at room temperature, but gentle heating is advisable if a substantial evolution of gas is desired.
Because of the risk of a runaway reaction, a round-bottom flask should be used.

3) Add formic acid little by little to gently heated sulfuric acid, never allowing the formic acid to exceed one-fifth of the initial volume of sulfuric acid.
Alternatively, the two acids may be mixed cold and then heated gradually over a gentle flame.

4) Heat a mixture consisting of 1 part potassium ferrocyanide and 3 parts concentrated sulfuric acid. This method, described in numerous chemistry books, is not recommended at all because a very similar reaction may give rise to hydrogen cyanide, a highly toxic substance that is extremely dangerous to inhale, even in small quantities.

IMPORTANT NOTE: Wash the gas first with water and then with a sodium hydroxide solution in order to retain any aceton, carbon dioxide, or acid vapours that may have been carried over. Dry the gas over solid sodium hydroxide

CARBON DIOXIDE OR CARBONIC ACID — CO_2

1) React dilute hydrochloric acid with white marble. It is usually recommended that the marble be as white as possible and free from veining in order to eliminate various gaseous impurities resulting from the action of the acid on certain metallic constituents sometimes present in the stone. In practice, however, it is not always easy to obtain perfectly white marble. It may readily be replaced by the white decorative pebbles and stones now sold in many home-improvement stores. These are often of even better quality than marble for this purpose.

2) React various acids with sodium or potassium bicarbonate or carbonate. Other carbonates may also be used, but they are considerably more expensive.

3) Prepare a mixture of oxalic acid (or an alkali oxalate) and powdered manganese dioxide. Add only a very small quantity of water and then allow sulfuric acid to fall onto the mixture. This is merely a laboratory curiosity, since the process is considerably more expensive and more complicated than the preceding methods.

4) Mix solid oxalic acid with hydrogen peroxide and heat gradually until the reaction proceeds regularly. This, too, is merely a laboratory curiosity, since the gas is then mixed with large quantities of water vapour and is not easily dried.

IMPORTANT NOTE: Dry the gas over calcium chloride or quicklime after first washing it with water or with a sodium bicarbonate solution.

SULFUR DIOXIDE OR SULFUROUS ACID — SO_2

1) Heat copper with concentrated sulfuric acid in a flask. The attack of the metal is often irregular at the beginning of the reaction and may then produce considerable foaming. It is therefore prudent to use vessels whose capacity is substantially greater than the volume occupied by the reagents.
NOTE: Copper turnings are frequently used for this preparation. Since they may be contaminated with machine oils that react with sulfuric acid to produce carbon dioxide and various organic compounds, it is advisable to wash the gas first with limewater and then with a suitable organic solvent.
The copper sulfate formed during the reaction may be recovered by precipitating it from its solution with alcohol and then allowing the alcohol to evaporate.

2) In the preceding experiment, replace the copper with mercury. As one might readily imagine, this is purely a laboratory curiosity in view of the cost of mercury.

3) A method providing a regular evolution of particularly pure sulfur dioxide consists of heating sulfur in concentrated sulfuric acid while carefully avoiding the boiling point. This is an excellent method whenever a very pure gas is required.

4) At room temperature, simply allow sulfuric acid to fall onto sodium sulfite moistened with a very small quantity of water. This last detail is absolutely essential, although it is never mentioned in chemistry books. If the acid is allowed to fall onto dry sulfite, a crust rapidly forms on the surface and strongly hinders the reaction. Thanks to the presence of a little water, the evolution of gas remains regular and continues for a much longer time. Care must nevertheless be taken not to add too much water, since sulfur dioxide dissolves in it and the evolution of gas then becomes unsatisfactory.

5) At room temperature, allow sulfuric acid to fall onto sodium metabisulfite or sodium bisulfite.
WARNING: Like sodium sulfite, both sodium bisulfite and sodium metabisulfite deteriorate when exposed to moist air. Solid sodium sulfite and sodium metabisulfite should therefore be stored in tightly sealed containers. Sodium bisulfite, which is available only as a liquid, must be kept in perfectly airtight bottles and protected from light.

6) Heat concentrated sulfuric acid containing a large excess of charcoal. A mixture of sulfur dioxide and carbon dioxide is then produced. This very economical method is really practical only when preparing a solution of sulfurous acid. Carbon dioxide dissolves only very slightly in aqueous sulfur dioxide (sulfurous acid), which makes the separation remarkably convenient. The gases should first be passed through a wash bottle containing a little water in order to retain any sulfuric acid that may have been carried over. They are then directed into a second bottle containing water that has previously been boiled and allowed to cool in the same tightly stoppered bottle. A solution of sulfurous acid is thus obtained very easily and at low cost.

IMPORTANT NOTE: Always dry sulfur dioxide with calcium chloride and wash it only with a very small quantity of water because of its solubility.

NITROGEN — N_2

In the past, chemists prepared relatively pure nitrogen by placing an animal under a large bell jar until it succumbed from lack of oxygen. The carbon dioxide thus produced was then removed by means of limewater. The gas remaining in the bell jar consisted essentially of nitrogen, although still mixed with the noble gases naturally present in the atmosphere. This method was every bit as cruel as the old practice of obtaining formic acid by distilling ants. Needless to say, such procedures have long since been abandoned and should be rejected even as laboratory curiosities.
In 1933, in a manual of chemical experiments, John Murray described another curious method for obtaining nitrogen. According to him, one merely had to heat animal muscle tissue in nitric acid. Judging from some of the other experimental procedures proposed by this author, however, the purity of the gases obtained was clearly not his principal concern...
Nitrogen is probably the least reactive of all the gases commonly used in an amateur laboratory, noble gases excepted. Preparing it therefore serves, in most cases, little purpose beyond a scientific demonstration or laboratory curiosity.

1) Heat a solution containing potassium dichromate and ammonium chloride.

2) Prepare two concentrated solutions, one of ammonium chloride and the other of sodium nitrite (or potassium nitrite) to which a small quantity of potassium dichromate has been added in order to suppress the evolution of nitric oxide. Immediately before the experiment, mix the two solutions and heat gently. When the evolution of gas becomes vigorous, reduce the heating or stop it altogether. The reaction will nevertheless continue for a considerable time.

3) Nitrogen may also be obtained by boiling a concentrated solution of ammonium nitrite.

4) Another method of preparing nitrogen relies on reactions from organic chemistry. Freshly prepared sodium hypobromite is used according to the procedure described before. It is allowed to flow into a dilute urea solution. The evolution of nitrogen is immediate, but the gas is accompanied by carbon dioxide, which must be removed by bubbling the mixture through limewater.

5) A variation of the preceding method consists of reacting sodium hypobromite with an aqueous ammonia solution or even with an ammonium chloride solution in the presence of sodium hydroxide.

6) Sodium hypochlorite solution is added to a fairly concentrated urea solution

placed on a magnetic stirrer. Nitrogen is evolved, unfortunately mixed with carbon dioxide. The latter may easily be removed by bubbling the gas through either limewater or a sodium hydroxide solution.

7) Another method consists of mixing aqueous ammonia with bleach. Very small bubbles of nitrogen are evolved, but only in very limited quantity. Water and a chloride are also formed. This procedure should nevertheless be regarded merely as a laboratory curiosity, since the yield is extremely poor.
NOTE: In view of what has just been explained in Methods 6 and 7, it is quite obvious that the foam produced after urination in a toilet bowl containing bleach does not constitute proof that a woman is pregnant, despite claims that can now be found on certain internet sites! In fact, the complex reaction between urine and bleach produces a variety of substances, including chlorine, nitrogen, carbon dioxide, and also toxic gases such as nitrogen trichloride (which is likewise formed in chlorinated swimming pools through contact with the perspiration of swimmers) and, in smaller quantities, cyanogen chloride.

8) Nitrogen may also be obtained by pouring a very dilute aqueous ammonia solution into bromine water, although the yield is extremely poor.

9) Another method, of interest mainly as a laboratory curiosity, consists of immersing a zinc strip in molten ammonium nitrate.

IMPORTANT NOTE: Always dry nitrogen with calcium chloride and wash it through dilute sulfuric acid containing potassium dichromate

NITRIC OXIDE (also called NITROGEN MONOXIDE) — NO

1) React copper with nitric acid previously diluted to a specific gravity of 1.2.
This concentration, together with maintaining the apparatus in an ice-water bath, is essential if one wishes to avoid the formation and evolution of other nitrogen oxides. The evolution of gas may be promoted by adding a few drops of a concentrated sodium nitrite solution to the flask containing the copper. Despite these precautions, the gas obtained will always contain a small amount of nitrogen dioxide. It may easily be purified by passing it through a Drechsel bottle containing a sodium hydroxide solution.
Recovering the copper nitrate formed during the reaction is not particularly convenient because it is a deliquescent salt. If one nevertheless wishes to attempt its recovery, the solution should be concentrated as far as possible by heating, then filtered and placed in a desiccator.

2) Allow sulfuric acid to flow into a concentrated solution of potassium nitrate containing copper turnings. This method is essentially equivalent to reacting freshly generated nitric acid with copper.

3) Dissolve 130 g of potassium nitrite in 500 mL of water and maintain the solution at 45 °C in a flask. A concentrated ferrous sulfate solution containing 10% concentrated sulfuric acid is then added gradually. The sulfuric acid may also be replaced by hydrochloric acid.

4) Add concentrated nitric acid drop by drop to a boiling solution of ferrous sulfate containing sulfuric acid. Suitable proportions are 50 g of ferrous sulfate, 50 mL of water, and 25 mL of concentrated nitric acid in a half-litre flask.

5) Bring to the boil a mixture of water, potassium nitrate, and sulfuric acid, then add a ferrous sulfate solution.
The ferrous sulfate may be replaced by ferrous chloride provided that the sulfuric acid is likewise replaced by hydrochloric acid.
NOTES:
a) With the exception of the first method, all the others are merely laboratory curiosities and are of little practical value. Even more exotic—or frankly extravagant—methods have been proposed. One example is the reaction suggested by L. W. Winkler, which consisted of treating a dilute mixture of potassium iodide and potassium nitrite with 50% sulfuric acid. Although very pure nitric oxide is indeed evolved, large quantities of iodine are also produced and can scarcely be removed except by means of a cold trap.
b) Whenever nitric oxide comes into contact with air, it will inevitably form nitrogen dioxide. The simplest way to prevent contamination is therefore to ensure that all vessels through which the gas is to pass have first been completely purged of air.
c) Nitric oxide may be accumulated in a fairly concentrated ferrous sulfate solution, with which it forms a brown complex. Simply heating the solution is sufficient to dissociate the complex and release the gas once again.
d) Since elevated temperatures should preferably be avoided when preparing this gas, an all-glass Kipp generator should be used only for filling small bottles or for short experiments that produce rapid results. In other cases, a simple apparatus should be preferred, with the main reaction flask maintained in an ice-water bath.

IMPORTANT NOTE: Dry the gas over concentrated sulfuric acid. It may be collected over strongly salted water.

NITROGEN DIOXIDE — NO_2
DINITROGEN TETROXIDE — N_2O_4
DINITROGEN TRIOXIDE (also called NITROUS ANHYDRIDE) — N_2O_3

Nitrogen dioxide is a red gas which, when associated with nitric oxide, most commonly forms a dimer of formula N_2O_4, that is to say a compound in which the two species are present in proportions that vary according to the physical conditions.

The $NO–NO_2$ mixture, when maintained at temperatures below –21°C, may also

form a trioxide of formula N_2O_3 . This compound loses its stability as soon as the temperature rises above that limit.

It was only shortly before the Second World War that the exact structures of these molecules were finally understood. This explains why considerable confusion exists in many older chemistry books regarding the names of these gases, the structures of their molecules, and even their methods of preparation.

Under their various forms, these compounds constitute what chemists traditionally referred to as red nitrous fumes or red fumes, which are evolved in a great many reactions involving nitric acid and nitrates. These fumes are extremely toxic and rapidly damage the lungs. They should therefore never be inhaled. Their colour, together with an odour somewhat reminiscent of chlorine, should immediately alert the experimenter to the danger involved.

1) In a porcelain dish, rapidly heat lead nitrate in order to dry it thoroughly. Mix it with thoroughly dried fine sand and place the mixture in a borosilicate glass tube (borosilicate 3.3 type). Heat continuously. The red gas evolved consists essentially of nitrogen dioxide. It cannot be collected over water because it reacts with it to form nitric acid.
NOTE: The sand is added so that the lead oxide formed during the reaction combines with the silica present in the sand rather than with that of the glass tube, which might otherwise be attacked and eventually perforated.

2) A simple way of obtaining the red nitrous fumes described in older chemistry books is to pass sulfur dioxide through concentrated nitric acid. A mixture of nitric oxide and nitrogen dioxide is then evolved, with nitrogen dioxide generally predominating. At the same time, sulfuric acid is formed in the liquid.

3) Allow concentrated sulfuric acid to fall gradually onto solid sodium nitrite.

4) N_2O_3 may also be prepared as follows. Place 6 g of starch in a 500 mL flask and pour over it 72 g of concentrated but non-fuming nitric acid. Heat the mixture very gradually. At a certain point, a vigorous evolution of N_2O_3 occurs. The gas may then be passed through a trap immersed in a mixture of ice and calcium chloride. The reddish gas readily condenses to form a green liquid. This liquid may be poured into a small beaker and water at room temperature added to it. Dense red nitrous fumes are then evolved, while a blue liquid consisting of unstable nitrous acid remains behind. The gradual fading of the blue colour provides a visible indication of the progressive decomposition of the acid.
NOTE: In Methods 3 and 4 above, depending on the experimental conditions, either N_2O_4 or N_2O_3 may be obtained.
WARNING: The action of concentrated nitric acid on starch (or on sugar, which may be substituted for it) may, under certain conditions, give rise to an explosive substance as well as small quantities of hydrogen cyanide. It is therefore important not only to ensure good ventilation but also to work behind a sturdy transparent

safety screen. In truth, this experiment should be carried out only with small quantities of material and solely as a matter of scientific curiosity.
When sugar is used instead of starch, the risk of explosion may be greatly reduced by heating concentrated nitric acid with a quantity of white sugar not exceeding one-fifth of the weight of the acid.
It should also be noted that if nitric acid is diluted with seven to eight times its volume of water, its prolonged action on starch at elevated temperature produces oxalic acid.

NITROUS OXIDE (commonly known as LAUGHING GAS) — N_2O

1) Heat solid sulfamic acid together with concentrated nitric acid. At a certain point, a vigorous evolution of gas begins and further heating is no longer necessary.
NOTE: Although little known, this method provides an easy and safe way of preparing nitrous oxide.

2) Heat ammonium nitrate carefully and uniformly until it melts, taking care never to exceed 250 °C, since an explosion hazard exists above 290 °C. Only small quantities should ever be used (approximately 30 g).
NOTE: The chemist Pelouze suggested a less dangerous variation, involving no risk of explosion, although the gas obtained is less pure. In this method, ammonium nitrate is heated in the presence of an excess of concentrated sulfuric acid.

3) Prepare an intimate mixture of solid ammonium chloride and sodium nitrite, then heat it to approximately 180 °C.
NOTE: This method is less well known and safer than the preceding one. Its principal drawback is that, in addition to sodium chloride, it produces a considerable quantity of water vapour that must be removed by means of a cold trap.

DANGERS OF "LAUGHING GAS"

The so-called laughing gas has now become one of the most widely used means by which young people seek access to various forms of "artificial paradise". Initially consumed from the small cartridges used in whipped-cream dispensers, it is now increasingly inhaled from large cylinders readily available through the Internet.

In addition to its euphoric effects, nitrous oxide becomes toxic when consumed in large quantities. Numerous cases of neurological injury have been reported, ranging from nerve damage and limb paralysis to death by asphyxiation.

Although nitrous oxide is still used in medicine today, it should, outside the chemistry laboratory, be administered only by physicians properly

PHOSPHINE (also called HYDROGEN PHOSPHIDE or PHOSPHANE) — PH_3

Two hydrogen compounds of phosphorus are generally encountered together: gaseous PH_3 and liquid P_2H_4 (diphosphine or diphosphane). In amateur or school laboratories, the preparation of PH_3, usually contaminated by a very small quantity of P_2H_4, is generally little more than an amusing laboratory curiosity, although it is not without danger. The procedure is as follows. Small pieces of yellow phosphorus are placed in a sodium hydroxide solution occupying most of the volume of a flask or Erlenmeyer flask fitted with a two-hole stopper. On one side, the vessel is connected to a tube whose end is situated just below the water level in a watertrough. On the other side, it is connected to a carbon dioxide generator. Carbon dioxide is first allowed to pass slowly above the sodium hydroxide solution (and not through it) in order to expel all the air present both in the reaction vessel and in the delivery tube leading to the trough. The flask is then heated. Little by little, small bubbles begin to appear. At that point, the carbon dioxide supply is stopped. The PH_3 produced gradually drives the carbon dioxide ahead of it until it finally emerges from the tube immersed in the trough. As soon as the first PH_3 bubble comes into contact with the air, it ignites spontaneously and a white cloud is formed. If the outlet tube is particularly well designed and maintained in a vertical position, this cloud may even assume the appearance of a smoke ring. At the same time, a distinct garlic odour becomes noticeable.

DANGER OF PHOSPHINE

It should be emphasized that it is dangerous to breathe either this gas or the substances produced by its combustion. The characteristic garlic odour therefore constitutes a genuine warning signal that should never be ignored, since no antidote exists for this poison. For this reason alone, the experiment should be carried out only outdoors, with the experimenter positioned so that the wind carries the products of the reaction away from him at all times.

PH_3 prepared in this manner is never pure. It is invariably contaminated by H_2 and P_2H_4, which renders it spontaneously flammable in air. To obtain PH_3 that is not spontaneously flammable, the P_2H_4 must be removed by severe cooling or the gas must be prepared from calcium phosphide decomposed by hydrochloric acid. Such procedures, however, are of no practical interest in an amateur or school laboratory.

The necessity of purging the apparatus before the evolution of the gas begins should now be obvious: it is simply to prevent a possible explosion within the apparatus should the phosphine encounter a pocket of air. Likewise, when the experiment has been completed and gas evolution has ceased, the apparatus should again be purged with carbon dioxide before the main flask is opened, thereby preventing any possible explosion.
NOTE: Later I shall describe another method of observing the spontaneous ignition

of a PH_3–P_2H_4 mixture, one that involves no danger of explosion whatsoever.

BORON TRIFLUORIDE — BF_3

Boron trifluoride is a toxic and corrosive gas with an extremely strong affinity for water. It has virtually no use in an amateur laboratory.
As a laboratory curiosity, it may be prepared by heating gently 1 part calcium fluoride, 1 part boric acid, and 12 parts sulfuric acid. As soon as bubbles begin to appear, the gas is collected by simple displacement of air in a thoroughly dry bottle. Because of its high density, this operation presents no difficulty.
When brought into contact with moist air, the gas produces dense white fumes. Certain substances, including some types of paper, have been reported to ignite in this gas because of its remarkable tendency to extract water from them, but I must confess that I never obtained such results during my own experiments, perhaps because the quantities involved were too small.

METHANE — CH_4

Since methane is the principal component of natural gas, it is seldom necessary to prepare it in the laboratory. Not everyone, however, has access to a natural gas supply...

1) Grind together in a mortar 1 part quicklime, 1 part sodium acetate, and 1 part potassium hydroxide. Mix the substances thoroughly and fill a test tube to approximately four-fifths of its capacity. Place the tube horizontally and begin heating near the open end, gradually moving the flame farther away from the opening. Once the test tube has become completely filled with methane, the gas may be ignited at the tip of a drawn-out glass tube passing through the stopper used to close the test tube. The test tube will often be lost, since part of the mixture melts and attacks the glass.

2) According to some authors, another method consists of immersing pieces of aluminium carbide in warm water. The difficulty is that aluminium carbide is extremely difficult to obtain. I have never had the opportunity to test this method myself and can therefore offer no useful comments regarding its practical value.

ACETYLENE — C_2H_2

To prepare this gas easily, it is usually recommended to allow water to fall onto pieces of calcium carbide, a substance that is readily obtainable but must always be kept perfectly dry. Some authors say it is nevertheless preferable to proceed in the opposite manner, that is to say, to begin with a certain quantity of water contained in a flask and then add the carbide through the neck, which can easily be opened and

closed. The reason for this is that the heat produced by the reaction in the presence of only a small quantity of water may, in certain circumstances, lead to an explosion. But of course, opening and closing the flask each time a new piece of carbide is added also introduces a small quantity of air, which may likewise create an explosion hazard if the gas is subsequently heated or ignited. The best solution is therefore to prevent excessive heating by immersing the flask in an ice-water bath and agitating it continuously, for example by means of a magnetic stirrer. The calcium hydroxide produced by the decomposition of calcium carbide nevertheless tends to form a thick slurry, which gradually slows the reaction. One way of improving the situation is to use a glucose solution instead of plain water.
WARNING: Commercial calcium carbide contains so many impurities that the acetylene obtained from it is generally contaminated by other gases, including hydrogen sulfide, phosphine, and even hydrogen arsenide (arsine), which give it a characteristic odour reminiscent of both garlic and rotten eggs. Since phosphine and arsine are toxic, it is advisable to avoid breathing acetylene prepared in this traditional manner.

IMPORTANT NOTE: In most cases, it is unnecessary to remove these impurities. If this nevertheless proves desirable, the gas may be washed through a copper sulfate solution, which will retain both hydrogen sulfide and hydrogen arsenide.

ETHYLENE — C_2H_4

While cooling vigorously and stirring continuously, slowly pour concentrated sulfuric acid into absolute ethanol in such a way that the acid is present in a quantity four to five times greater than that of the alcohol. The mixture is then heated in the presence of pumice fragments to ensure a more even distribution of heat. The temperature must be maintained between 160 °C and 180 °C. At approximately 140 °C, ether is produced, whereas above 180 °C a mixture of carbon dioxide and sulfur dioxide is evolved.
WARNING: Acid vapours should be removed by passing the gas through a wash bottle containing a sodium hydroxide solution. The ether should in turn be retained in a wash bottle containing cold concentrated sulfuric acid. Because of the formation of explosive ether vapours, this experiment should be attempted only by an experienced amateur chemist equipped with complex apparatus of excellent quality.

ETHYL CHLORIDE (or CHLOROETHANE) — C_2H_5Cl

First prepare a mixture consisting of 1 part ethyl alcohol and 1 part sulfuric acid, adding the acid to the alcohol (and not the reverse) while stirring continuously and cooling vigorously. This mixture is then poured into a flask containing 2 parts sodium chloride, after which the flask is heated gently.

IMPORTANT NOTE: Hydrogen chloride is formed simultaneously and must be

removed by passing the gas through a Drechsel bottle containing a small quantity of water.

METHYL NITRITE — CH_3NO_2

In an Erlenmeyer flask closed by a two-hole stopper, place a mixture consisting of an aqueous sodium nitrite solution and methyl alcohol. The stopper carries both a dropping funnel and an outlet tube terminating in a swan-neck delivery tube. Through the funnel, an aqueous sulfuric acid solution is added drop by drop. Bubbles of methyl nitrite are evolved. Allow the apparatus to purge itself completely of the air originally present, then ignite the gas at the end of the swan-neck tube. It burns with a luminous blue-yellow flame.

NOTE: For the amateur chemist, the preparation of this gas is merely a laboratory curiosity and has no practical value beyond the ignition experiment described above.

4.3 The Equipment to Use

Traditionally, chemistry books indicate that a gas may be produced simply by using any suitable vessel fitted with a two-hole rubber stopper. One hole accommodates an ordinary dropping funnel, while a simple delivery tube passes through the other and leads, if necessary, to a wash bottle or a drying column. In practice, however, such an arrangement is suitable only when the gas produced is intended to react with another gas or with only a very small quantity of liquid. Indeed, a rubber stopper becomes hard and brittle after prolonged contact with halogens, nitric acid vapours, and the various gaseous oxygen compounds of nitrogen.

There is also another practical disadvantage. When the gas produced must subsequently pass through substantial quantities of liquid, the pressure required may exceed that needed to force the liquid back into the dropping funnel. In such cases, opening the stopcock may result either in the liquid refusing to flow from the funnel or in its being violently expelled by the excess pressure. This can be extremely dangerous.

Figure 57

For these reasons, a different type of apparatus should always be used. This consists of a cylindrical dropping funnel fitted with a stopcock, but also provided with a side arm connecting its upper section to the portion located between the stopcock and the ground-glass joint (Figure 57).

This special funnel may be used in several different ways. It may be fitted to a filtering Erlenmeyer flask, allowing the gas produced to escape through the lateral side arm, or mounted on a two-neck flask, the second neck being reserved for the gas outlet. An even simpler arrangement consists of closing the

upper part of the funnel with a stopper fitted with a tube serving as the gas outlet.

4.3.1 Collecting a Gas by Displacement of Air

In certain circumstances, it is necessary to have a volume of gas enclosed within a vessel such as a large test tube (commonly called a gas jar), a bottle, a flask, or an Erlenmeyer flask of substantial capacity. As we shall see, such vessels may be filled in two different ways.

When the gas is significantly heavier than air (for example Cl_2 , CO_2 , HI, HBr, or BF_3), it may easily be collected by displacement of air by allowing it to "fall" into a thoroughly dry vessel held vertically with its opening facing upward. A simple watch glass placed over the mouth of the vessel is then generally sufficient to close it.

Conversely, lighter-than-air gases such as ammonia or hydrogen may be collected by allowing them to "rise" into a thoroughly dry vessel held vertically with its opening facing downward. The vessel is then closed with an ordinary stopper until required for use.

These two methods are obviously imperfect, since they do not guarantee that the vessel will be filled completely and with certainty. Nevertheless, in the practice of an amateur laboratory, they generally prove entirely satisfactory.

4.3.2 Collecting a Gas by Displacement of a Liquid

A gas may readily be collected by displacement of a liquid whenever one is certain that it neither reacts with that liquid nor dissolves in it.

The technique consists of introducing the gas into the lower part of a receiving vessel previously filled with the chosen liquid and placed in a trough partially filled with the same liquid. As the gas enters the vessel, it gradually displaces the liquid contained within it. In practice, for many gases, a trough (which may be nothing more than a large dish or even a medium-sized aquarium) is filled with water. One or more gas jars, or larger vessels likewise filled with water, are then inverted in the trough. For chlorine, strongly salted water is used because the gas cannot readily dissolve in it.

The real difficulty often lies in keeping these vessels securely in place while they are being filled, so that they neither slip nor break. Many chemists simply hold them by hand, but this leaves only one hand free and may prove inconvenient. Early chemists devised two ingenious accessories that unfortunately no longer appear in most modern laboratory catalogues.

The first was a porcelain trough somewhat resembling a wooden shoe and shaped internally in such a way that the vessel intended to receive the gas could be placed in it in stable equilibrium (Figure 58). This trough was especially valuable when mercury was used as the collecting liquid, because its internal shape made it possible to reduce considerably the quantity of this expensive metal required.

Figure 58

The second accessory, far lighter and less cumbersome, was a gas support, a small hollow dome made of porcelain or earthenware and provided with both a slot and an opening through which the delivery tube carrying the gas could pass. The support was simply placed on the bottom of the trough, where it provided a stable base upon which receiving vessels could be balanced. At the extreme right of Figure 58, one of these accessories may be seen.

The trough shown in the illustration, although only of medium size, already measures 33 centimetres in length. One can therefore readily appreciate the advantage offered in many situations by the gas support, which generally measured only 8 centimetres in diameter, and sometimes even less, while remaining extremely light. A competent handyman could easily construct such a support today from any material denser than water. As for vessels intended to be filled with gas, the best solution is generally to secure them by means of clamps attached to a laboratory stand.

NOTES ON AQUEOUS MINERAL SOLUTIONS

One might suppose that preparing an aqueous solution is simply a matter of dissolving a salt in distilled water. In practice, however, the situation is somewhat more complicated.

It should be remembered that water gradually absorbs oxygen and, more importantly, carbon dioxide from the atmosphere. As a result, it slowly becomes acidic and effectively turns into a very dilute solution of carbonic acid capable of reacting with certain salts. This effect is particularly noticeable when preparing solutions of copper, lead, manganese, or ferrous salts. As these salts dissolve, the solution may gradually develop a cloudiness or even a precipitate that becomes increasingly pronounced, eventually giving the liquid a whitish appearance in the case of copper or lead salts, a brownish appearance with manganese salts, or a yellowish appearance with ferrous salts. In the first cases, basic carbonates of copper, lead, or manganese are formed; in the latter, ferric compounds result from oxidation of the ferrous salt.

The best way to avoid these difficulties is to boil the distilled or demineralized water beforehand, dissolve the salt while the water is still hot, and immediately stopper the bottle afterward. Naturally, as the solution is used and the liquid level falls, air—and therefore carbon dioxide—will enter the container. In practice, carbon dioxide is not a major problem because its concentration in air is relatively low, and the solution will therefore be only slightly affected. Oxygen-sensitive solutions, however, such as those containing ferrous salts or alkaline sulfides, present a more serious challenge.

Chemists have proposed various methods to overcome this difficulty. One approach consists of covering the surface of the solution with a layer of paraffin oil or ether in order to isolate it from the atmosphere. Such methods, however, also have their drawbacks. Personally, I would recommend flushing the upper part of the bottle with argon before closing it. Because argon is heavier than air, it forms a protective blanket over the solution. Small argon cylinders fitted with simple pressure regulators are now readily available from many hardware stores and welding suppliers in the world.

It should also be remembered that certain aqueous solutions cannot be stored for long periods and should therefore always be prepared fresh. Typical examples include solutions of tartaric acid, which rapidly develop mold growth, as well as starch paste, potassium permanganate, lead acetate, and mercury(II) chloride solutions.

Finally, some salts do not tolerate direct dilution in water. They undergo immediate hydrolysis and may even produce precipitates. Examples include antimony chloride, mercury(II) nitrate, and tin(II) chloride. Such salts should be dissolved in water previously acidified with the same acid from which the salt is derived.

Chapter 5 - Useful Preparations

This chapter presents a number of useful recipes and practical notes for preparing mineral substances, mixtures, and solutions that are commonly required in the laboratory.

PHENOLPHTHALEIN

Grind together 2.35 g of phthalic anhydride, 3 g of phenol, and 1 g of zinc chloride until a homogeneous mixture is obtained. Transfer the mixture to a test tube and heat it for about five minutes in an oil bath maintained at 180 °C. The contents will melt during this period. Remove the test tube from the oil bath and allow it to cool. Then add a mixture of water and ethyl alcohol. Phenolphthalein has thus been prepared.

A single drop added to an alkaline solution immediately produces a magenta coloration. The product obtained may not be completely pure or colorless. It may exhibit a slight orange or pink tint. This is of little consequence when it is intended for use as an indicator for alkaline solutions.

SODA LIME AND POTASH LIME

Both soda lime and potash lime are efficient absorbers of carbon dioxide.

Soda lime is prepared by slaking quicklime with a concentrated sodium hydroxide solution, using approximately one part by weight of sodium hydroxide for every two parts by weight of quicklime. The resulting mass is then heated to red heat in a steel or porcelain crucible in order to drive off all remaining water. After cooling, it should be stored in a tightly sealed PVC container, since the material gradually attacks glass.

Potash lime is prepared in exactly the same manner, except that potassium hydroxide is used instead of sodium hydroxide.

ALCOHOLIC POTASH

Dissolve approximately 20 g of potassium hydroxide (KOH) in 20–25 mL of water, then add 500 mL of 97% ethanol. Allow the mixture to stand undisturbed for about three days so that the potassium carbonate present can settle to the bottom. The clear liquid is then decanted into a clean container.

This reagent should be stored only for short periods, protected from both light and air, preferably in black PVC bottles. With time, the solution gradually deteriorates and acquires a brownish coloration.

SULFURIC ACID–ALCOHOL MIXTURES

In organic chemistry, it is often necessary to prepare mixtures of sulfuric acid and an alcohol. Such mixtures must always be prepared in the following manner. Place the alcohol in a vessel that has been thoroughly cooled, preferably in an ice-and-salt bath. Then add the sulfuric acid very slowly while stirring continuously.

This procedure is essential because it minimizes unwanted chemical reactions between the two substances during preparation. Such reactions may subsequently interfere with the intended use of the mixture.

The mixture should be used as soon as possible after preparation, since its composition gradually changes on standing.

TINCTURE OF IODINE

Tincture of iodine, now largely replaced in medicine by other disinfectants, was once routinely supplied in brown glass bottles. That was an unfortunate mistake. Indeed, Sapin and Popiel demonstrated many years ago that the interaction between these two components slowly produces hydriodic acid, ethyl iodide, and iodoform. All of these unstable compounds are very rapidly decomposed by light, thereby releasing... iodine! Tincture of iodine should therefore be stored in colorless glass bottles and certainly not in the dark. To prepare it, mix a certain quantity of iodine with 90% alcohol.

LOGWOOD TINCTURE

Heat pieces of logwood in distilled water for about ten minutes. Decant the liquid and cool it as rapidly as possible. Then add one and a half volumes of alcohol for each volume of the colored aqueous solution obtained. Store the preparation in an inactinic bottle.

48% HYDROBROMIC ACID SOLUTION

I have already described an earlier method for preparing hydrobromic acid. Here is another.

Pass an excess of sulfur dioxide (SO_2)—that is, continue until the reaction has unquestionably ceased—through a bottle containing a concentrated bromine-water solution maintained at 0 °C in an ice-water bath. The liquid gradually becomes lighter in color until it reaches a pale yellow shade. At this stage, it contains a mixture of hydrobromic acid and sulfuric acid in solution. The mixture is then distilled, and the fraction boiling at 125 °C is collected. This is a 48% hydrobromic acid solution.

Unlike hydriodic acid solutions, which tend to decompose rather rapidly, this reagent can be stored for long periods in a well-stoppered amber bottle.

NITROUS OR FUMING NITRIC ACID

Fuming nitric acid is difficult and hazardous to buy and to store. Since it is only occasionally required, it is generally preferable to prepare small quantities shortly before use.

To do so, take a given weight of potassium nitrate and add 3 g of starch for every 100 g of nitrate. Place the mixture in an all-glass distillation apparatus. Quickly add concentrated sulfuric acid in a weight ratio of approximately 1.5 to 2 parts acid per part nitrate. The reaction begins immediately, after which the temperature should be raised promptly in order to distill the product, while keeping the temperature below 125 °C.

Sodium nitrate may also be used. In that case, suitable proportions are approximately 25 g of $NaNO_3$ and 30 g of H_2SO_4 .

Because of the added starch, the acid that distills over is strongly enriched with nitrogen dioxide (NO_2). The product obtained is therefore not strictly speaking fuming nitric acid but rather nitrous nitric acid, which is often equally effective—or even more effective—than the ordinary fuming nitric acid supplied by industry.

Pure fuming nitric acid may be prepared by distilling ordinary nitric acid mixed with three times its volume of concentrated sulfuric acid. Only half of the original nitric acid is collected. This fraction is then mixed with an equal volume of concentrated sulfuric acid and distilled once more. During this second distillation, somewhat less than the full volume of nitric acid employed is recovered. The procedure is therefore both laborious and expensive because of the quantities of reagents required. It is best reserved for situations where only a small amount of pure fuming nitric acid is needed.

Another, more efficient but considerably more complex method consists of distilling nitric acid together with thoroughly dried potassium nitrate. In this case, both pressure and temperature must be kept as low as possible, requiring suitable vacuum equipment. In addition, severe bumping may occur, making it necessary to employ a large and sturdy reaction vessel. I do not recommend this procedure for the amateur laboratory.

AQUA REGIA

Aqua regia is a mixture of hydrochloric acid and nitric acid. The name dates back to the age of the alchemists and even earlier. It is one of the few chemical reagents capable of dissolving gold.

Opinions differ considerably regarding the proportions to be used. Recipes range from one volume of hydrochloric acid and half a volume of nitric acid to one volume of hydrochloric acid and three volumes of nitric acid. Regardless of the proportions employed, the liquid gradually turns yellow and then reddish while evolving chlorine gas. The important point is that it is a continuously evolving mixture that cannot be stored. It should therefore be used as soon as possible after preparation. Under no circumstances should aqua regia be sealed in a bottle because of the chlorine gas it continually releases.

This extremely reactive mixture is sometimes used to clean laboratory glassware. For the same purpose, some chemists employ a nitric acid–sulfuric acid mixture instead.

There is also another form of aqua regia, much less well known than the preceding one. It is prepared by mixing one part nitric acid with two or three parts hydrobromic acid. The mixture rapidly turns yellow, then red, and evolves red bromine vapors. A distinction should therefore be made—although few authors do so—between chloride aqua regia (hydrochloric aqua regia) and bromide aqua regia (hydrobromic aqua regia).

When gold is introduced into the mixture aqua regia, a solution generally described as chloroauric acid is produced. Such a solution is inherently unstable unless gold is present in excess until dissolution has completely ceased—a procedure that would obviously be prohibitively expensive.

OXALIC ACID

Place starch in a bottle and carefully pour concentrated, but non-fuming, nitric acid over it. Within approximately ten hours, the starch disappears and the liquid acquires a faint yellow coloration. If the mixture is then stirred, reddish vapors appear and the yellow color becomes more pronounced. When a portion of the

liquid is heated gently, large quantities of brown nitrogen oxide fumes are evolved, leaving behind white crystals of oxalic acid. An aqueous solution of these crystals readily decolorizes potassium permanganate solution.

In principle, however, oxalic acid is prepared by slowly heating one part of sugar or starch with eight parts of nitric acid. When the reaction is complete—that is, when gas evolution has ceased—the liquor deposits oxalic acid crystals upon cooling.

SELENIOUS ACID

In a small Erlenmeyer flask, heat nitric acid with pieces of selenium. Large quantities of reddish-brown fumes are evolved. When the selenium no longer reacts, transfer the liquid to a test tube and heat it while rotating the tube. The greenish liquid rapidly becomes colorless and, after the water has evaporated, a white powder remains. This is selenious acid or selenium dioxide, depending on the temperature reached. Add water to obtain a solution of selenious acid.

CHROMIC ANHYDRIDE [CHROMIUM(VI) OXIDE]

Prepare a saturated solution of potassium dichromate in an Erlenmeyer flask. Then add concentrated sulfuric acid in small portions, with constant stirring, until the volume of acid added is approximately one and a half times the original volume of the dichromate solution. The mixture becomes very hot, and continuous cooling is advisable. Chromic anhydride begins to form when the color of the liquid suddenly changes and numerous small, sparkling crystals of a deep red color with a slight violet hue appear. Continue adding an excess of sulfuric acid, which does not interfere with the preparation. The mixture is then rapidly filtered through a fritted-glass funnel connected to a filter flask under moderate vacuum.

Obtaining the product completely dry is scarcely possible outside an industrial setting. The prepared material should therefore be stored in a tightly sealed container, since both chromic anhydride and the sulfuric acid adhering to it readily absorb moisture from the air.

Some authors recommend washing the crystalline paste with concentrated nitric acid until no reaction with barium chloride can be detected, indicating the absence of sulfate ions, and then heating the product until all vapors have disappeared. Since chromic anhydride decomposes upon heating, however, this procedure entails a significant risk and may simply replace sulfuric acid contamination with nitric acid contamination.

Consequently, the only practical way to obtain perfectly dry chromic anhydride is to purchase it from a specialized supplier.

CHROMOSULFURIC ACID MIXTURE

This liquid is also used primarily for cleaning laboratory glassware.

Dissolve 60 g of potassium dichromate ($K_2Cr_2O_7$) in a mixture prepared from 80 g of concentrated sulfuric acid and 270 g of water. The resulting liquid is as fluid as water. With time, crystals may form in the solution.

One author recommends a different preparation. Approximately 500 mL of concentrated sulfuric acid is heated to about 150 °C until the first white fumes appear. Finely powdered potassium dichromate is then added in small portions until, in this case, a syrup-like liquid is obtained. This requires approximately 80 g of dichromate.

Whenever this preparation is employed, always pour the syrupy mixture into water and never the reverse.

SODIUM HYPOBROMITE SOLUTION

First Method
Mix one volume of sodium hydroxide solution having a specific gravity of 1.33 with twice its volume of water. Then slowly add one-tenth of that original volume of bromine while stirring thoroughly, preferably with a magnetic stirrer. The reaction mixture should be kept very cold, for example by using crushed ice, in order to prevent the formation of bromate.

Second Method
Dissolve 7.7 g of sodium hydroxide in 80 mL of water and allow the solution to cool. Transfer the solution to a 100 mL volumetric flask, add 1.9 cm^3 of bromine, dilute to the calibration mark with water, and mix thoroughly using a magnetic stirrer. When all the bromine has disappeared, the solution is ready for use.

NOTE: The final solution should have a golden-yellow color. It should be stored in a tightly sealed amber-glass bottle, protected from light and kept in a cool place. Even under these conditions, however, it does not keep well. It is therefore always preferable to use it fairly quickly, or better still, freshly prepared.

SODIUM ALUMINATE

To prepare a sodium aluminate solution, place a number of small balls made from aluminum foil into a solution of sodium hydroxide (caustic soda).

CAUTION: This reaction can accelerate rapidly and generates a considerable amount of heat. In addition, if a glass vessel is used, it may become permanently corroded.

For this reason, a ceramic container is preferable.

After several hours, the reaction will have ceased. During this period, large quantities of hydrogen are evolved, so all flames and other ignition sources must be strictly avoided. At the end of the reaction, a few partially attacked aluminum balls generally remain, and a black deposit will be found at the bottom of the vessel. Filter the mixture promptly, either through filter paper or, preferably, through a fritted-glass funnel. The resulting liquid is colorless, perfectly clear, and strongly alkaline. It should be stored in PVC bottles.

The solution reacts with acids and ammonium salts to produce a gelatinous precipitate of aluminum hydroxide, which should not be confused with aluminum oxide (alumina).

Limewater produces a gelatinous precipitate of calcium aluminate.

If carbon dioxide is passed through the sodium aluminate solution, a white precipitate of hydrated aluminum hydroxide forms very rapidly.

INCREASING THE CONCENTRATION OF HYDROGEN PEROXIDE

It is easy to increase the concentration of a dilute hydrogen peroxide solution (for example, 8-volume). Simply place it in a freezer and remove the ice cubes (water) that form. This method, however, does not make it possible to obtain a solution stronger than about 20-volume.

TIN(II) CHLORIDE, formerly "stannous chloride", $SnCl_2$ AND TIN(IV) CHLORIDE, formerly "stannic chloride", $SnCl_4$

Tin(II) chloride is prepared by allowing an excess of tin to react with concentrated hydrochloric acid while applying gentle intermittent heating. When the reaction is complete, the mixture is boiled in order to expel excess hydrochloric acid. The resulting solution may be stored as obtained or diluted with four times its volume of water previously acidified with 1/20 of its volume of hydrochloric acid.

The storage bottle should contain a small amount of metallic tin and should be protected from contact with air. Even under these conditions, tin(II) chloride gradually absorbs oxygen from the air or dissolved in the water and is slowly converted into tin(IV) chloride.

Tin(IV) chloride is prepared in two ways.

First method :
Thoroughly dried chlorine gas is passed over heated tin contained in a

borosilicate-glass tube. The end of the tube should be fitted with a standard ground-glass joint connected to an adapter leading to a well-dried receiving flask kept strongly cooled. Once the tin has become "ignited" external heating may be discontinued, as the reaction thereafter sustains itself. The liquid that distills over was historically known as Libavius's Fuming Liquor, after the chemist Andreas Libavius who described it. The name also refers to the dense white fumes produced when the liquid comes into contact with moist air.

Second method :
A straight water-cooled Liebig condenser fitted with standard ground-glass joints is mounted vertically in a clamp. A small glass retaining piece shaped like a thumbtack—or, failing that, a few glass beads—is first introduced into the inner tube in order to prevent little objects from falling through. The tube is then filled with tin granules. The condenser is connected to a supply of cold running water. Beneath it, a small two-neck flask, preferably pear-shaped, is placed so that one neck fits directly into the lower ground-glass joint of the condenser. Through the second neck, a stream of chlorine gas, previously dried by passage through a tall column of anhydrous calcium chloride, is introduced. The female joint at the top of the condenser is connected to a Drechsel bottle containing a sodium hydroxide solution intended to absorb excess chlorine.

The cooling water is started first in order to cool the inner tube thoroughly, after which chlorine generation is begun. As soon as chlorine enters the condenser, sparks become visible. The tin then appears to melt while boiling vigorously, and a yellow liquid flows into the receiving flask. A small amount of white fume escapes from the top of the apparatus and comes into contact with the sodium hydroxide solution. The liquid in the Drechsel bottle gradually becomes milky, and a substantial white deposit eventually appears.

The reaction is complete when all of the tin has disappeared.

The chlorine supply is then shut off, and the various parts of the apparatus are disconnected progressively, taking care that both the receiving flask and the condenser remain tightly closed. The condenser should be disconnected last.

During dismantling, abundant white fumes will be observed. These consist of hydrated tin compounds formed when atmospheric moisture reacts with traces of tin(IV) chloride present throughout the apparatus. Each piece of equipment should be rinsed under running water as soon as possible in order to minimize the formation of these toxic fumes, which may cause severe respiratory injury and potentially lead to pulmonary edema.

The product obtained is liquid tin(IV) chloride, usually tinted yellow by dissolved excess chlorine. Using a pipette, transfer a small quantity of the liquid and allow it to fall drop by drop into a 100 mL beaker half-filled with distilled water at room temperature. Each drop produces a sound similar to that of a red-hot piece of metal

plunged into water. At first, the drops sink and resemble small transparent crystals. These then disappear while bubbles are evolved.

A solution of hydrated tin(IV) chloride ($SnCl_4 \cdot 5H2O$) has thus been formed and may be stored for future use. If the chloride is mixed with a much larger quantity of water, hydrolysis occurs, producing hydrochloric acid and hydrated tin oxide.

If the tip of the pipette is examined carefully, a small mass of white crystals can often be seen forming gradually. These crystals subsequently disappear as they absorb moisture from the air, once again producing white fumes.

IMPORTANT NOTE: It is advisable to continue the reaction until all of the tin has been consumed. Any remaining tin tends to adhere strongly to the walls of the condenser and can only be removed by treatment with hydrochloric acid or a mixture of hydrochloric and nitric acids (aqua regia), a cleaning operation that may require considerable time.

COPPER(I) CHLORIDE (formerly "cuprous chloride" CuCl)

First Method:
Heat together one part copper(II) sulfate, one part metallic copper, two parts sodium chloride, and ten parts distilled water, acidified with a few drops of hydrochloric acid. Boil the mixture until the liquid becomes colorless or, more commonly, until only a greenish-brown coloration remains. While still hot, pour the liquid into twenty times its volume of previously boiled water, acidified with 1/20 of its volume of hydrochloric acid. The boiling removes dissolved air from the water. White copper(I) chloride precipitates immediately and rapidly settles to the bottom of the vessel. Decant most of the liquid and add a fresh large quantity of boiled cold water in order to wash the precipitate thoroughly. After allowing it to settle once more, remove as much water as possible and immediately dissolve the salt either in hydrochloric acid or in aqueous ammonia.

In hydrochloric acid solution, copper(I) chloride is theoretically colorless. It rapidly acquires a greenish-brown coloration through reaction with atmospheric oxygen. It is therefore advisable to store the solution in a tightly stoppered bottle containing loosely packed copper turnings. If the presence of metallic copper causes the solution to become colorless again, so much the better. Over time, however, the solution may gradually be converted into the green hydrochloric solution of copper(II) chloride.

The ammoniacal solution is likewise theoretically colorless but rapidly turns blue through oxidation. Since it is difficult to remove dissolved air from commercial ammonia solutions, one way of avoiding this coloration is not to dissolve the salt directly in liquid ammonia. Instead, ammonia gas may be bubbled through the boiled water used for the final washing of the precipitate. This procedure, however,

requires working from the outset in a carbon dioxide atmosphere.

A simpler alternative consists of storing the blue solution in a tightly stoppered bottle filled with loosely packed copper turnings. The solution gradually becomes colorless once again.

Ammoniacal copper(I) chloride solution is the classical reagent for acetylene, producing a brick-red precipitate of copper acetylide.

WARNING: This precipitate must never be allowed to dry, as it may become dangerously explosive.

To obtain dry copper(I) chloride, proceed as follows. After precipitation with a large excess of boiled water, allow the solid to settle and decant as much water as possible. Then touch the moist mass with filter paper so that capillary action removes much of the remaining water. Absolute alcohol is then poured over the precipitate in order to absorb the residual moisture. After decantation, most of the liquid is removed and replaced with fresh absolute alcohol. This operation is repeated several times until the water has probably been eliminated completely. The alcohol is then largely removed and replaced with ether. After settling, the ether-alcohol mixture is decanted and fresh ether added. This operation is likewise repeated several times in order to remove all traces of alcohol. Finally, the ether is allowed to evaporate rapidly, leaving dry copper(I) chloride.
Evaporation may be accelerated while simultaneously limiting contact with air by passing a stream of thoroughly dried carbon dioxide over the ether.

It should also be noted that replacing sodium chloride with potassium bromide in the above procedure yields copper(I) bromide instead of copper(I) chloride.

Second Method:
An excess of copper may be heated in concentrated hydrochloric acid to which a few drops of nitric acid have been added. Additional hydrochloric acid and a few drops of nitric acid are introduced periodically as the reaction proceeds. The resulting solution has a characteristic greenish-brown color and consists of copper(I) chloride dissolved in hydrochloric acid. If chlorine gas is passed through the cooled solution, copper(II) chloride is formed.

Third Method:
Another very simple procedure consists of preparing two saturated solutions of equal volume, one of sodium chloride and the other of copper(II) sulfate. When the two solutions are mixed, a green liquid containing both sodium sulfate and dissolved copper(I) chloride is obtained. If this liquid is poured into a large volume of previously boiled water containing a small amount of acetic acid, white copper(I) chloride precipitates.

Fourth Method:

Prepare approximately half a liter of water containing generous amounts of copper(II) sulfate and sodium chloride, without paying particular attention to the exact concentrations. A bright green solution is obtained. Pass sulfur dioxide through the liquid until the reaction is complete. The solution becomes brown.

When this solution is poured into a large quantity of previously boiled and cooled water containing a little acetic acid, a substantial quantity of insoluble white copper(I) chloride precipitates.

FERROUS SULFATE [Fe (SO4)] AND FERROUS CHLORIDE (FeCl2) SOLUTIONS

Even in the crystalline state, ferrous sulfate is difficult to preserve. Upon exposure to air, it rapidly oxidizes and acquires a yellow coloration. Fortunately, it is inexpensive and readily available from garden suppliers, where it is still widely sold as a moss-control treatment. It is best purchased in transparent plastic packaging after verifying that the pale green crystals do not contain yellow or brown agglomerates, which would indicate partial oxidation and impurity. Once the package has been opened and a portion of the crystals removed, the remainder should be stored in a bottle fitted with a greased ground-glass stopper and a stopcock allowing a high vacuum to be maintained. Storing the salt in an ordinary vacuum-sealed plastic bag of the type used for frozen foods is entirely inadequate.

To prepare a solution of ferrous sulfate—or, more rarely, ferrous chloride—begin by boiling completely demineralized water in order to remove dissolved air. While still very hot, pour the water into a bottle containing the ferrous salt and fitted with an airtight stopper. The bottle should be filled completely up to the neck and then closed immediately. As the solution cools, the liquid contracts and a partial vacuum forms above it. Ideally, the entire solution should be used on the same day and should not be stored for extended periods, since it slowly deteriorates through contact with water alone. If it is necessary to keep the solution for two or three days while withdrawing small portions on several occasions, a layer of ether approximately 5 mm thick may be poured over the surface. This protects the solution from atmospheric oxygen as the bottle gradually empties. Samples should then be withdrawn with a pipette.

In many situations, teachers replace the unstable ferrous sulfate solution with a more stable substitute.

To prepare the first of these substitutes, dissolve a small quantity of impure ferrous sulfate—which may already contain some ferric sulfate—in water. The water need not even be boiled beforehand. A cloudy yellowish solution is obtained. A large amount of sulfur dioxide is then bubbled through the liquid and the bottle is closed and allowed to stand. Gradually, the solution clears by sedimentation and acquires the characteristic pale green color of ferrous sulfate solution. The clear liquid is then transferred to a smaller bottle, taking care not to disturb the yellowish-brown

deposit that has formed. The large excess of dissolved sulfur dioxide is sufficient to preserve the solution indefinitely. Strictly speaking, this liquid is not a pure ferrous sulfate solution, but for teaching purposes it is perfectly suitable for many demonstration experiments that would normally require one.

One might suppose that the same approach could be used to prepare a stable substitute for ferrous chloride from the much more common ferric chloride. In practice, however, the following reaction occurs:

$$2FeCl_3 + SO_2 + 2H_2 \rightarrow FeSO4 + FeCl_2 + 4HCl$$

(see Mellor, J. W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London–New York, 1930, Vol. 10, pp. 231–232). The resulting solution is therefore an acidic mixture of ferrous sulfate and ferrous chloride rather than a pure ferrous chloride solution and it offers no real advantage.

Here is another way to prepare ferrous chloride... Prepare a solution of iron(III) chloride and boil it for a few minutes with iron filings. Cool it briefly under running water, pass a stream of carbon dioxide or argon through the flask to prevent oxidation, and stopper it. After allowing the solid to settle, a colorless solution is obtained, or a faintly green one if the original iron(III) chloride solution was concentrated. Add a few drops of sodium hydroxide solution. A green, gelatinous precipitate is formed, indicating that the iron(III) chloride has been converted into iron(II) chloride.

In teaching school laboratories, ordinary ferrous sulfate solution is often replaced by a solution of ferrous ammonium sulfate. Both the crystalline salt and its aqueous solutions are readily preserved without any special protection from atmospheric oxygen. Like the sulfur dioxide-stabilized substitute described above, however, this second substitute is not suitable for every experiment that can be performed with ordinary ferrous sulfate, particularly those involving chloride-containing compounds.

At this point, both an ethical and a pedagogical question arises. In situations such as those described above, where a teacher uses one substance in place of another, it is up to the teacher to decide whether or not to reveal the substitution to the students. Certain "pedagogical fictions" may occasionally be useful—but only for a limited time. Otherwise, the trust between teacher and students may ultimately be undermined.

MERCUROUS(I) NITRATE — $Hg_2(NO_3)_2$

To prepare mercurous nitrate, allow an excess of mercury to react with nitric acid diluted with half its volume of water and cooled in an ice bath. The operation should be carried out in the open air, since abundant reddish-brown fumes are evolved and should not be inhaled. Allow the reaction to proceed until white crystals begin to form. Remove any remaining mercury and store the product in this form.

The crystals may subsequently be dissolved in a small quantity of hot water, but they decompose if an excessive amount of water is used. It is therefore preferable to dissolve them in a small quantity of nitric acid. Such a strongly acidic solution may then be diluted further with water if desired.

One author recommends the following method for obtaining the salt in solid form. Mix 30 g of mercury with 50 mL of water and then add 50 mL of 53% nitric acid. At the end of the reaction, warm the mixture gently. If all the mercury has not dissolved, or if a yellow coloration or a yellow precipitate of mercury oxide appears, add a further drop of nitric acid. The solution is then heated gently until its volume has been reduced to approximately 20 mL. Allow it to cool and then place it in an ice bath in order to precipitate the maximum quantity of salt. Next, add twice its volume of ice-cold aceton. The resulting crystals are collected and allowed to dry in air on filter paper.

Millon's reagent is derived from mercurous nitrate. It may be prepared by mixing 10 mL of mercury with 188 mL of nitric acid (specific gravity 1.42). If necessary, warm gently toward the end of the reaction and then dilute the green liquid with twice its volume of water. When an organic substance is heated to 50–55 °C with this reagent, a brick-red precipitate is produced if tyrosine is present. Tyrosine occurs, for example, in bananas, almonds, and milk.

MERCURIC(II) NITRATE — $Hg(NO_3)_2$

Mercuric nitrate is prepared by reacting mercury with hot nitric acid and then evaporating the solution until it acquires a syrupy consistency.

The abundant reddish-brown fumes evolved during this operation must not be inhaled.

COPPER CARBONATE

Prepare a solution of copper sulfate in a flask and gradually add a solution of sodium carbonate or potassium carbonate. A pale blue precipitate forms, accompanied by the evolution of large quantities of carbon dioxide, causing the liquid to foam. After allowing the precipitate to settle, add a little more alkaline carbonate solution if the supernatant liquid still retains a blue coloration due to dissolved copper sulfate. It is preferable, however, to proceed by repeated decantation, transferring the liquid successively to other vessels. In this way, one can avoid adding an excessive amount of carbonate solution. Finally, collect the entire precipitated mass, decant once more, and wash it with water. The precipitate may then be boiled in a fresh quantity of water. It gradually turns green, yielding the green pigment known as malachite, which was formerly used by painters.

The experiment may be concluded at this point. Alternatively, hydrochloric acid may be added gradually until the precipitate dissolves. When dissolution is nearly complete, decant the resulting emerald-green liquid and dilute it with water. The solution then becomes blue. Copper(II) chloride has thus been obtained. If desired, it may be isolated by evaporation and crystallization.

SODIUM OR AMMONIUM SULFIDE (AND POLYSULFIDE) SOLUTIONS

Begin with a solution of sodium hydroxide in previously boiled and cooled water (from which dissolved air has been removed) or, alternatively, with a solution of aqueous ammonia, depending on the sulfide to be prepared.

Divide the solution into two approximately equal portions, one being about 5 to 10% larger than the other. Pass hydrogen sulfide through the smaller portion until saturation is complete. A colorless hydrosulfide solution is thereby formed. It possesses a strong rotten-egg odor, retains a certain amount of dissolved hydrogen sulfide,while the hydrosulfide itself gradually decomposes by hydrolysis upon exposure to moist air. The second portion of the original solution, which has been kept aside, is then added to the first. A theoretically neutral solution of a colorless sulfide ion (S^{-2}) is thus obtained, although a slight excess of alkali remains present.

This solution should be stored in tightly sealed PVC bottles. Such storage minimizes contact with air and prevents the alkaline solution from slowly attacking and opacifying glass.

Despite every precaution, these solutions eventually deteriorate and are therefore best used when freshly prepared. Their decomposition is indicated first by a progressively more yellow coloration, due to the formation of polysulfides, and later by the appearance of a deposit of elemental sulfur. At that stage, the solution becomes particularly useful for dissolving sulfur deposits that may adhere to the walls of vessels in which various chemical reactions producing sulfur have taken place.

A similar result may be obtained more rapidly in either of two ways. The first consists of adding a small quantity of sulfur directly to the freshly prepared, theoretically neutral sulfide solution. The second consists of boiling flowers of sulfur in an aqueous solution of sodium or potassium hydroxide and filtering the resulting yellow or brown liquor after it has cooled. The latter solution, however, also contains thiosulfate.

Four additional points deserve mention:
a) It is preferable to cool the solution while hydrogen sulfide is being introduced. This may be done simply by placing the bottle in an ice-water bath.
b) The initial solution should not be excessively concentrated. The more concentrated it is, the more hydrogen sulfide will be required to produce the

hydrosulfide. More importantly, there is a risk that the liquid may solidify into a mass of crystals, thereby preventing the reaction from proceeding to completion.
c) The storage bottle should be filled as completely as possible because these solutions deteriorate through absorption of atmospheric oxygen. The effect becomes increasingly pronounced as the contents are used and the volume of air above the liquid increases.
d) If the PVC bottle is perfectly airtight, there is a good chance that it will gradually deform as oxygen is absorbed and the internal pressure decreases. Care should therefore be taken that such deformation does not lead to cracking of the container.

A layer of liquid paraffin may be used to isolate the solution from the air contained in the bottle, but this method is rather inconvenient. When suitable equipment is available, the air space above the liquid may instead be replaced with argon.

FINAL NOTE: If a truly neutral sulfide solution is required, the best approach is to dissolve crystalline sodium sulfide obtained from a specialized supplier in previously boiled and cooled water.

POTASSIUM OR SODIUM THIOCARBONATE (SULFOCARBONATE)

First Method:
Dissolve 50 g of potassium hydroxide in 200 mL of water and divide the solution into two slightly unequal portions. Saturate the smaller portion with hydrogen sulfide and then combine it with the larger portion. A solution of potassium sulfide is thus obtained (see the preceding preparation for further details). Add 30 g of carbon disulfide (CS_2) and allow the mixture to stand for approximately twelve hours. The mixture is then heated under reflux for one hour and left to stand. Crystals of thiocarbonate gradually separate.

WHAT DOES "HEATING UNDER REFLUX" MEAN?

A liquid is said to be heated under reflux when it is boiled in a flask fitted with a vertical condenser that is open to the atmosphere but continuously cooled. The vapors therefore condense and continually return to the flask. In this way, although the liquid remains at its boiling point, its total volume does not decrease.

Second Method:
Place equal volumes of carbon disulfide and an aqueous solution of potassium or sodium hydroxide in a tightly stoppered bottle. Shake and allow the mixture to stand. The carbon disulfide forms the lower layer. As the hours pass, the upper aqueous layer gradually turns orange and then orange-red owing to the formation of thiocarbonate.

Third Method;
Begin by preparing a solution of sodium monosulfide (see the preparation described above). Carbon disulfide is then added in the proportion of eight parts to eleven parts of sodium monosulfide. Immediately place the vessel in a water bath maintained at 40–50 °C and stir vigorously with a magnetic stirrer. A red coloration gradually develops. When it has become intense, transfer the mixture to a separatory funnel and remove everything that does not possess this characteristic color.
NOTE: The orange-red coloration obtained by these two methods indicates that the thiocarbonate remains mixed with monosulfide and is therefore impure. These preparations should thus be regarded as laboratory curiosities rather than practical methods of preparation.

Fourth Method
Pure thiocarbonate may be obtained by applying the principle of the second method, but using a solution of sodium hydroxide in alcohol. Care must be taken that the solution is not excessively concentrated, otherwise it will be necessary to employ a large excess of carbon disulfide. The mixture is stirred with a magnetic stirrer. A yellow layer containing the thiocarbonate gradually rises to the surface. The excess carbon disulfide is then rapidly evaporated. This may be accomplished in the open air with the aid of a fan or a hair dryer operated on its cold setting.

CALCIUM THIOCARBONATE (SULFOCARBONATE)

Take a 100 mL bottle fitted with an airtight stopper and introduce a quantity of limewater or baryta water. Add an equal volume of carbon disulfide. Allow the mixture to stand, with or without occasional shaking. Thiocarbonate gradually forms and produces a yellow coloration in the upper portion of the two liquid layers. This yellow layer may be collected and the carbon disulfide allowed to evaporate in order to observe briefly the yellow salt obtained, which decomposes in air like other thiocarbonates.
It should be noted that some chemists consider the product formed under these conditions to be not a thiocarbonate, but rather a hydroxythiocarbonate.

MAGNESIUM THIOCARBONATE (SULFOCARBONATE)

The preparation follows the same principle as that used for calcium thiocarbonate, except that a suspension of magnesium hydroxide is employed.

AMMONIUM THIOCARBONATE (SULFOCARBONATE)

Begin by saturating a quantity of absolute alcohol with thoroughly dried ammonia gas in a large separatory funnel. Then add an amount of carbon disulfide

corresponding to approximately one-tenth of the volume of alcohol originally used. Close the funnel and invert it. Open the stopcock and miix by gentle shaking, avoiding excessive agitation. Close the stopcock and return the funnel to its normal position. It is then closed with a stopper carrying a safety tube. The liquid gradually becomes yellow, warms spontaneously, and finally deposits sulfur-yellow crystals of ammonium thiocarbonate. Depending on the temperature, the reaction may proceed either quietly or quite vigorously. Some authors recommend cooling the funnel in melting ice, although this precaution is not really necessary. When the reaction is complete, allow the excess liquid to drain away, wash the crystals two or three times with ether, and again remove the surplus liquid (Figure 59).

Beautiful crystals of ammonium thiocarbonate may also be obtained by using 90–94% alcohol instead of absolute alcohol. In that case, the reaction proceeds more slowly and the crystals generally appear only after an hour or more.

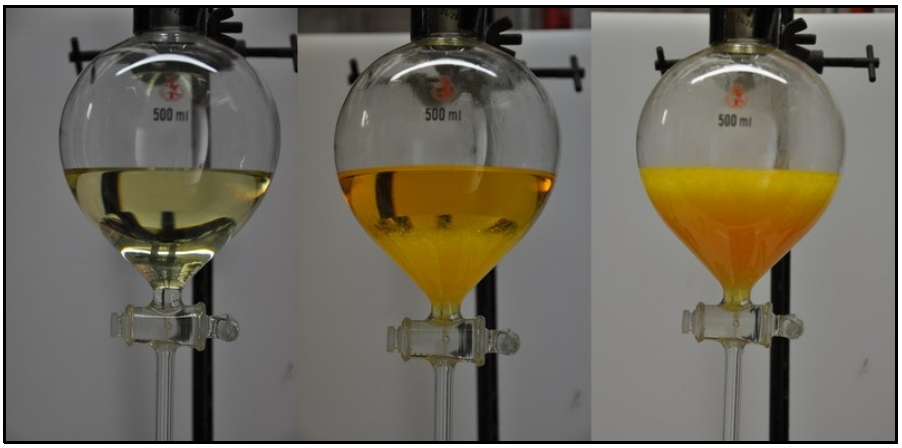


Figure 59

A NOTE ON THIOCARBONATES (SULFOCARBONATES)

As explained earlier, thiocarbonates cannot be stored in crystalline form when exposed to air. They rapidly decompose while releasing hydrogen sulfide. Aqueous thiocarbonate solutions are likewise unstable. They quickly become reddish and then brown. Such solutions should therefore always be used when freshly prepared.

For this reason, it is preferable to store the yellow crystals obtained by certain preparations beneath a generous layer of ether and to prepare aqueous solutions only as needed. The crystals may conveniently be removed from their container by means of a pipette whose tip has been cut off. Nevertheless, even when stored beneath a layer of ether, the crystals do not remain stable for more than a few weeks.

SODIUM OR POTASSIUM THIOCYANATE (SULFOCYANATE)

These salts are, par excellence, the reagents for ferric compounds, with which they produce a characteristic blood-red coloration. They may be prepared by either of the following methods.

First Method:
Heat sodium cyanide in a porcelain crucible. As soon as it begins to melt, add an excess of powdered sulfur. The sulfur ignites, evolving a considerable quantity of sulfur dioxide. Stir the mixture with a glass rod and discontinue heating. Without undue delay, pour the still-burning liquid into distilled water to a depth of approximately 3 cm and then filter. Additional useful material may be recovered by washing the cooled crucible with a small quantity of water. The resulting solution is perfectly suitable for its intended use.

Second Method:
Mix 46 parts of potassium ferrocyanide, 32 parts of sulfur, and 17 parts of potassium carbonate in a porcelain crucible. Heat the mixture to red heat until it becomes molten and begins to evolve bubbles. Remove the crucible from the flame, allow it to cool, and crush the solid mass obtained. Transfer the material to ethyl alcohol and heat for several minutes in a water bath until boiling. The mixture is then allowed to cool. Colorless crystals of thiocyanate gradually separate from the solution.

IMPORTANT NOTE: Aqueous solutions of these salts are unstable and should therefore be used fairly soon after preparation. In the solid state, the salts are also deliquescent.

Some chemists prefer to store the potassium thiocyanate they have prepared in alcohol and dissolve it in water only when needed.

For occasional laboratory use, however, it is generally more convenient to obtain the solid salts from a specialized supplier and prepare the aqueous solution shortly before use.

Chapter 6 - High Solubility of Certain Gases

One of the best-known experiments illustrating the high solubility of certain gases in water is the classic demonstration known as the chemical fountain. Frequently described in chemistry books, it generally consists of inverting over a water trough a flask previously filled with gaseous ammonia (NH_3) or hydrogen chloride (HCl). The first drops of water entering the flask are supposed to dissolve the entire volume of gas almost instantly. The resulting partial vacuum then created draws the remaining water violently into the flask, producing what appears to be a fountain inside the vessel itself.

Unfortunately, this experiment often performs rather poorly in practice and is truly convincing only to those who are easily satisfied. In most cases, the flask fills only halfway with water. Such a result falls far short of demonstrating that the high solubility of the gas is capable of producing a substantial vacuum within the flask. The reason is simple: it is extremely difficult to fill a flask completely with ammonia or hydrogen chloride merely by displacing the air it contains. In reality, the flask always ends up containing a mixture of gas and residual air.

The method described below makes it possible to perform this experiment successfully and in a highly convincing manner.

The apparatus consists essentially of a gas-generating flask together with suitable drying equipment, a large tank containing water colored with an appropriate pH indicator, and a transparent vertical cylinder approximately 3 to 5 cm in diameter and about 40 cm high. This cylinder is the key element of the experiment.

After being thoroughly dried, the gas is introduced into the cylinder. Ammonia is admitted through the top, whereas hydrogen chloride is introduced through the bottom. The procedure described below applies to ammonia.

The vertical cylinder is closed at both ends with rubber stoppers, each pierced by two holes. Ammonia enters through a glass stopcock inserted into one of the holes in the upper stopper. Because ammonia is lighter than air, it gradually descends

through the cylinder, displacing the air and eventually leaving through a glass tube passing through one of the holes in the lower stopper. This outlet tube is fitted with a second stopcock connected to flexible tubing leading to a fume hood or suitable exhaust system. The second hole in the lower stopper contains a glass tube extending approximately 8 cm into the cylinder and slightly constricted at its upper end. This tube is connected by means of rigid-walled flexible tubing, such as vacuum tubing, to the water tank, where it extends well below the water surface. The submerged end is closed not with a stopcock but with a rubber stopper. This arrangement allows water to enter much more rapidly when the stopper is removed.

The second hole in the upper stopper carries a dropping funnel fitted with a stopcock and containing a small quantity of water.

The experiment itself consists of three distinct stages.

A)
With both the inlet and outlet stopcocks open, ammonia is introduced through the top of the cylinder. The gas flow is maintained for a sufficient time to ensure that all the air trapped within the apparatus—including the gas generator and drying train—has been completely displaced. At this stage the cylinder contains only ammonia. The inlet and outlet stopcocks are then closed, the gas generator is immediately disconnected from the rest of the apparatus, and it is placed in a well-ventilated location.
NOTE: If a three-way stopcock is used as the gas inlet valve, the generator need not be moved. Such a stopcock allows any gas still being produced to be diverted directly to a fume hood or exhaust duct.

B)
Once the cylinder has been completely filled with ammonia, two or three drops of water are allowed to fall into it through the dropping funnel. The stopcock of the funnel must be operated very carefully so that all of the water is not drawn in at once. Two or three drops are entirely sufficient to dissolve the ammonia trapped in the cylinder and thus create a strong partial vacuum.

C)
Only then should the rubber stopper sealing the tube immersed in the water tank be removed. Water is immediately drawn into the cylinder with a clearly audible sucking sound and rises almost to the very top. The cylinder will not fill completely because the connecting tube initially contains a small amount of air. Consequently, the shorter this tube is, the smaller the remaining air space will be.

As mentioned earlier, the water in the tank should contain a suitable colored indicator. The experiment becomes even more impressive when a distinct color change occurs as soon as the incoming water comes into contact with the aqueous ammonia solution formed inside the cylinder (Figure 60).

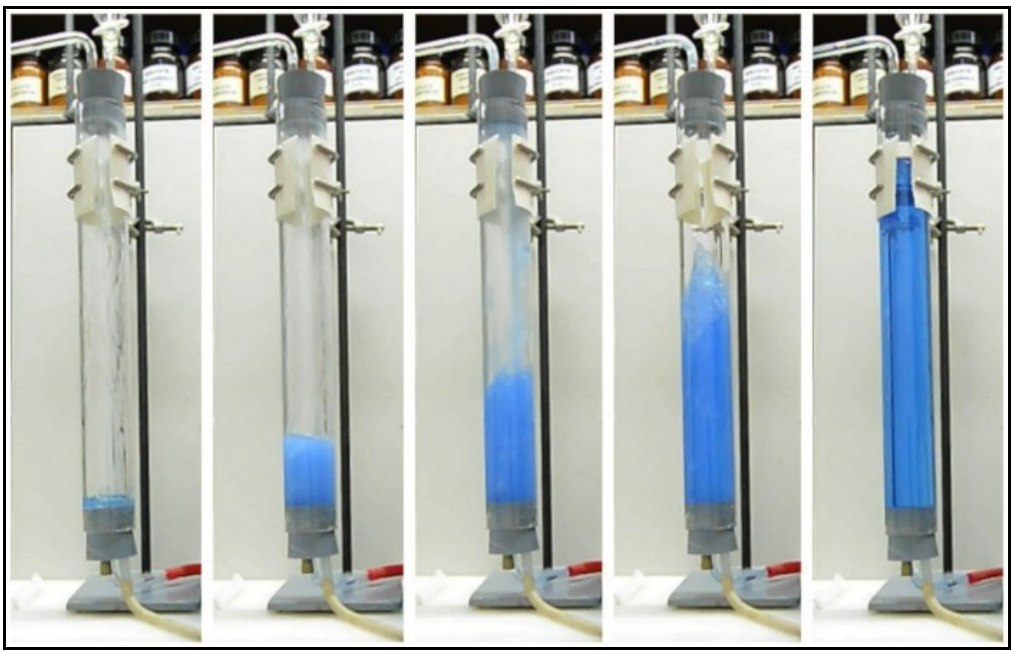


Figure 60

The same general procedure can be adapted for hydrogen chloride. Since this gas is heavier than air, it should be introduced through the bottom of the cylinder rather than through the top so that it displaces the air as completely as possible.

It goes without saying that the main cylinder, as well as all the tubing, stopcocks, and glass tubes used in the apparatus, must be perfectly dry before the experiment begins. Particular care should therefore be taken to plug the tube connected to the water tank before immersing it in the water.

Instead of the large cylinder described above, the experiment may also be carried out in a conventional gas bulb consisting of a relatively wide tube constricted at both ends and fitted with stopcocks. Since such bulbs generally have a rather limited volume, they are less suitable for demonstrations intended for a large audience, such as a classroom. They are, however, quite useful for illustrating the color changes produced when a suitable indicator comes into contact with water containing dissolved ammonia or hydrogen chloride.

Figure 60 presents a photographic summary of the experiment performed in a cylinder using ammonia and water containing bromothymol blue. Figure 61, on the following page, shows the same experiment carried out in a gas bulb immersed in water containing phenolphthalein.

A similar experiment can also be performed with carbon dioxide, although it is far less well known because it is considerably less spectacular. A large flask is first filled with carbon dioxide by downward displacement and then closed with a stopper carrying a bromine bulb filled with limewater. The stopcock of the bulb is opened, and gentle pressure is applied with a rubber bulb to force the limewater into the flask, where a white precipitate forms immediately.

Before the bulb has completely emptied, its stopcock is closed and the entire assembly is inverted over a water trough. The partial vacuum created within the flask is sufficient to draw water upward into it. Although simple in principle, this experiment requires a certain amount of dexterity.

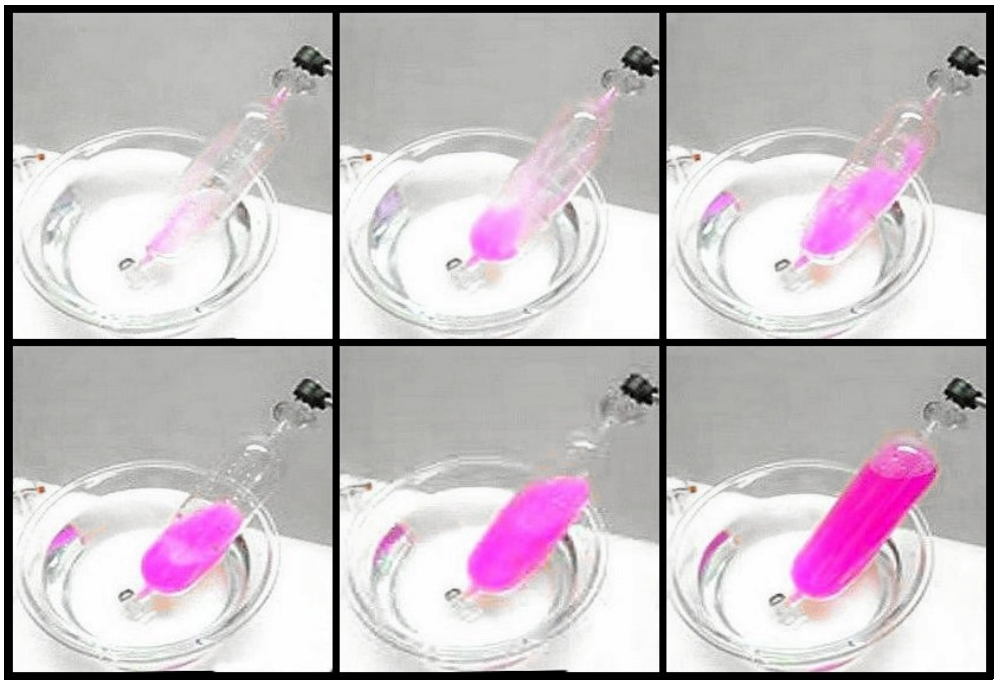


Figure 61

Here is another Experiment Demonstrating Gas Solubility...

Fill a flask of at least two liters capacity with chlorine gas and drop a cube of ice into it. Immediately close the flask with a one-hole stopper carrying a thermometer that has previously been allowed to reach the temperature of both the room and the flask. The ice cube will melt more rapidly than an identical cube placed in a similar flask containing only air. A slight decrease in temperature can also be observed on the thermometer. This experiment is not particularly significant and should be regarded merely as a laboratory curiosity.

Another instructive experiment may be carried out using a series of U-tubes. Each tube is filled with water —that has been boiled and then cooled while protected from contact with the air— so that the water level rises slightly above the highest point of the bend. Different gases are then bubbled through the various tubes: NH_3, HCl, HI, HBr, H_2S, CO_2, and SO_2. The pH of the resulting solutions is subsequently tested with indicator strips. It will be found that the last six gases produce acidic solutions, whereas ammonia yields a strongly alkaline one.

Each solution is then boiled separately and its pH tested again. Some of the solutions return to a nearly neutral condition, whereas others do not. The differences observed provide a useful illustration of the varying affinities that these gases exhibit toward water.

Chapter 7 - Combustion of Gases

AMMONIA

There are a few special cases in which gases that are normally considered non-combustible can nevertheless burn. Ammonia provides an interesting example.

- Pour concentrated aqueous ammonia into a test tube approximately 20 cm high and about 25 mm in diameter until the liquid reaches a depth of 6 to 7 cm. Through a tube reaching to the bottom of the test tube, introduce a steady stream of oxygen. After a short time, place a flame at the mouth of the tube. Either a flame will appear and may descend almost to the surface of the liquid, or a barking sound will be heard, similar to that produced when a hydrogen–oxygen mixture is ignited at the mouth of a small test tube (Figure 62).

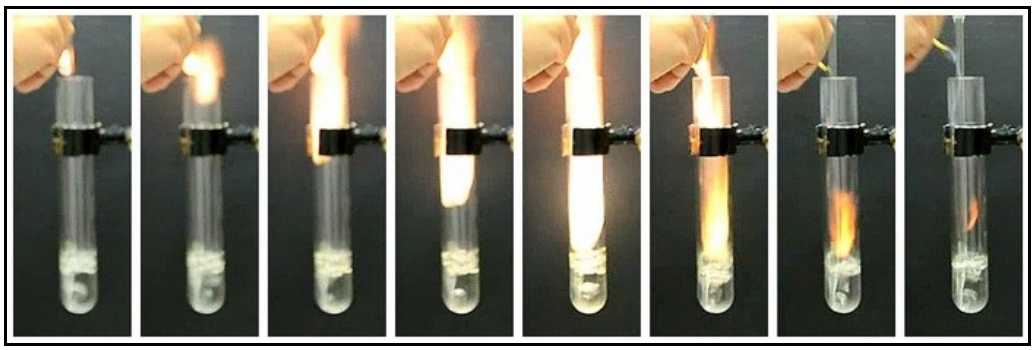


Figure 62

HYDROGEN

- The most classical experiment with hydrogen consists of collecting a small amount of the gas in a test tube held at an upward angle in front of the delivery tube. The test tube is then immediately brought near a flame. A characteristic barking sound is heard, caused by the small explosion that occurs when hydrogen mixed with air

is ignited, or even strongly heated. This demonstrates why apparatus containing hydrogen must ALWAYS BE THOROUGHLY PURGED before any part of it is heated or before a flame is brought near its outlet. In such circumstances, suitable safety goggles or a face shield are absolutely essential.

AN ESSENTIAL PRECAUTION

Most combustible gases detonate to a greater or lesser extent when mixed with air and exposed to a flame. Before bringing any generator producing a combustible gas near a flame, it is therefore essential to ensure beyond doubt that all air originally present in the apparatus has been completely displaced.

- Another classic demonstration consists of filling soap bubbles with hydrogen. A clay or PVC pipe is generally used for this purpose and dipped into a solution of water, detergent, and a small amount of glycerol. The bubbles rise rapidly, demonstrating that hydrogen is much lighter than air. They may also be ignited by carefully bringing a lighter close to them.

- The following experiment requires a certain degree of dexterity.
Once the generating flask has been thoroughly purged of air, ignite the hydrogen emerging from a finely drawn delivery tube. The flame is pale blue and difficult to see. Carefully place a small bell jar over the flame, ensuring that the very hot flame does not come too close to the glass, which could crack. Droplets of water soon form and run down the inner walls of the bell jar. The experiment should not be continued for too long because the hydrogen flame is so hot that it may soften the glass delivery tube and eventually seal it shut.

Figure 63

- The following procedure demonstrates the so-called chemical harmonica. Hydrogen is ignited at the end of a vertical glass tube at least 50 cm long. A second glass tube, 40 to 50 cm long, is held by its upper end and moved vertically up and down around the first tube and the flame above it. Depending on the position of the outer tube relative to the flame, various sounds are produced by the rapid movement of hot gases and air within the tube. Successful operation may require trials using tubes of different diameters. Although the flame itself changes little in intensity, it gradually acquires a reddish colour because its temperature is high enough to soften the glass (Figure 63).

The experiment was sometimes called the chemical organ because skilled demonstrators appear to have performed it

using several tubes simultaneously, producing a combination of different tones that were considered harmonious. One author once stated that the same experiment could be performed using carbon monoxide instead of hydrogen. My own attempts to reproduce this claim were unsuccessful, even when using tubes with diameters ranging from 1 to 5 cm. In my opinion, the failure is explained by the much lower flame temperature of carbon monoxide, which produces far fewer gaseous turbulences within the tube. Whether that author actually obtained positive results or merely assumed that such results should occur remains uncertain. The latter possibility seems plausible, since no other author known to me has reported success in producing the chemical harmonica effect with carbon monoxide.

- Fill a strong glass bottle or Erlenmeyer flask of 1 to 2 litres capacity with chlorine by simple displacement of air. Because chlorine is denser than air and coloured, the progress of the operation can easily be observed. When the vessel is visibly full of chlorine, cover it with a watch glass. Prepare a small hydrogen generator by placing hydrochloric acid and a few pieces of zinc in a flask. Once all air has been displaced from the apparatus, ignite the hydrogen emerging from a long delivery tube bent downward and introduce the burning jet into the chlorine-filled vessel. The hydrogen continues to burn in the chlorine with a flame that is more visible than in air. Sometimes, the characteristic sound associated with the hydrogen organ can be heard. After a short time, remove the burning tube and again cover the vessel that originally contained the chlorine, first adding a small quantity of water with a wash bottle. Shake well, then uncover the vessel to allow any remaining chlorine to escape. A test with silver nitrate reveals the presence of chloride ions, while indicator paper shows that the liquid is strongly acidic. Hydrochloric acid has indeed been formed.

Should the hydrogen flame accidentally go out while inside the chlorine vessel, the hydrogen delivery tube must be removed IMMEDIATELY. Failure to do so may allow the formation of a hydrogen–chlorine mixture capable of exploding under the influence of light alone (see page 144). For this reason, it is prudent to perform the experiment under subdued lighting and never in direct sunlight.

- In a similar manner, ignite hydrogen at the end of a delivery tube and introduce the burning jet into a flask filled with bromine vapour. The hydrogen continues to burn, producing a faint yellow flame (Figure 64). At the same time, the orange bromine vapour gradually disappears and is replaced by dense white fumes caused by the reaction of hydrogen bromide with moisture in the air. When the orange vapour has almost completely vanished, add a small quantity of water to the flask and shake it. The resulting solution is found to be acidic.

Figure 64

- Pass a stream of hydrogen through a small wide-necked flask fitted with a three-hole stopper. Through the first opening, the gas enters near the bottom of the flask; through the second, it

leaves from the top. The third opening carries a dropping funnel with its stopcock closed. The lower part of the funnel is filled with water in order to prevent air from entering when the stopcock is opened, since such an air intake could cause an explosion. A small quantity of benzene is placed in the upper part of the funnel.
Once the entire apparatus has been thoroughly purged of air, ignite the hydrogen leaving the flask. The flame is only faintly visible. Allow the water to enter the flask, followed by a few drops of benzene. The hydrogen flame immediately becomes bright, yellowish, and smoky.

CARBON MONOXIDE

- Like hydrogen–air mixtures, carbon monoxide–air mixtures explode when brought into contact with a flame. One therefore waits until all air has been displaced from the apparatus before igniting the gas at the end of its delivery tube. The flame observed is pale blue.

ACETYLENE

- Acetylene–air mixtures are likewise explosive. The gas should therefore only be ignited at the end of a drawn-out delivery tube once it is certain that all air has been removed from the generating flask. The flame is bright, yellowish-red, and produces abundant black smoke. When collected beneath a bell jar or on the surface of a plate, this soot is found to consist of carbon.

- By means of a rubber bulb, gently blow air directly into the base of the flame where it emerges from the tube. The flame becomes blue and much less smoky. This acetylene–oxygen combustion is the principle underlying certain welding torches. Comparison with the operation of a Bunsen burner supplied with natural gas (methane) is instructive.

ETHYL CHLORIDE (CHLOROETHANE)

- Ethyl chloride may be ignited directly as it leaves the reaction vessel. It may also be collected in a well-cooled gas trap, since it liquefies at about 11°C, and the liquid thus obtained can then be poured into a small crystallizing dish resting on an ice pack and ignited. In both cases, the combustion produces significant quantities of gaseous hydrogen chloride. This can easily be demonstrated by opening a bottle of aqueous ammonia near the flame: dense white fumes immediately appear. If a moistened indicator paper is passed rapidly through the flame, it will show a strongly acidic reaction. In the amateur laboratory, this gas offers little additional experimental interest beyond these observations.

Chapter 8 - Reactions Between Gases

8.1 With at Least Hydrogen

- Allow a sulfurous acid (H_2SO_3) solution to flow through the safety funnel of a two-neck flask used as a hydrogen generator. Hydrogen sulfide is soon evolved and can be detected either by its odor or with filter paper moistened with lead acetate solution, which immediately turns black.

8.2 With at Least One Halogen

I_2 + Cl_2

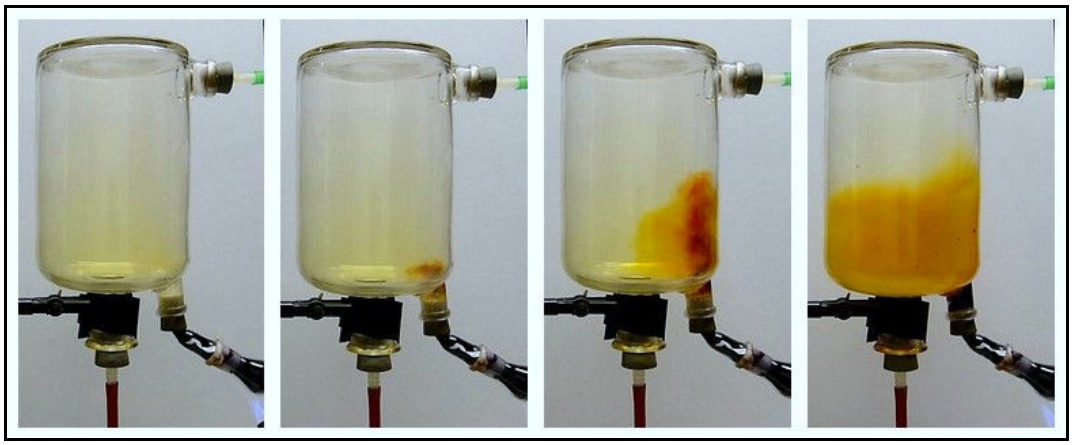


Figure 65

- In a flask fitted with three tubulures, chlorine is introduced, preferably from below, so that the gas gradually fills the entire vessel. Iodine vapor is then admitted through the second tubulure. It is obtained by gently heating a small flask containing solid iodine. Here (Figure 65) a Woulff bottle was used. Chlorine was introduced through the main tubulure, at the bottom center, while iodine entered directly from a small

heated bulb at the lower right. The external outlet was provided by the tubulure at the upper right. Iodine trichloride, ICl_3, forms at once. Its color may range from yellow to brown, with orange intermediate shades, depending on the form taken by its crystals. These crystals remain stable in an atmosphere of chlorine, especially if the flask is sealed at the end of the experiment, but they decompose rapidly in air once the flask is opened and the chlorine escapes. They dissolve readily in carbon tetrachloride, giving a red-brown liquid without altering the solvent. They also dissolve in ether, carbon disulfide, and alcohol, but in these solvents gradual alteration occurs. Dissolution is also possible in benzene, without modification of the solvent.

A second procedure consists in placing a little iodine in a bulb tube, then passing through it a stream of chlorine that has first been thoroughly dried by passage through a calcium chloride column. The iodine slowly begins to liquefy, taking on a reddish-brown color. Oily iodine monochloride, ICl, is then formed, with evolution of heat (Figure 66). At this stage, the tube is stoppered and placed for a few minutes in a freezer. The monochloride then sets to a red mass, since it solidifies at about 10 °C. This mass is dissolved in water, giving a yellow liquid, after which ether is added. The ether extracts the monochloride and forms a red upper layer (Figure 67).

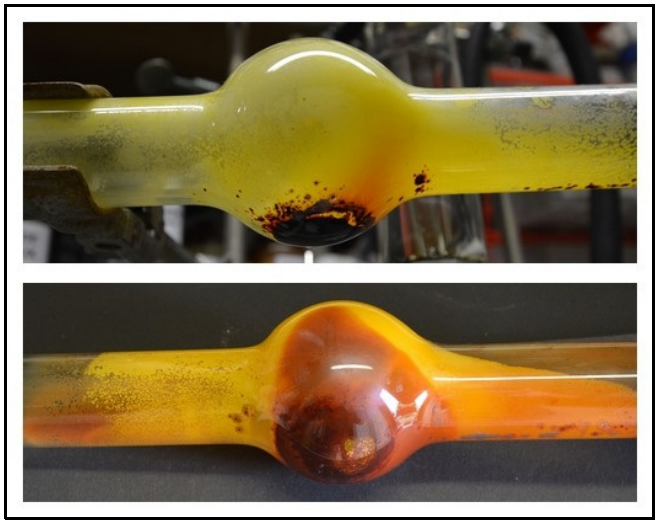


Figure 66

Figure 67

If, instead of stopping at this point, the passage of chlorine through the bulb tube is continued, the excess gas produces lemon-yellow iodine trichloride, ICl_3 , which coats the walls of the tube.

Br_2 + Cl_2

- One may allow a drop of bromine to fall into a flask of chlorine and observe that it gives a yellow liquid which evaporates rapidly. One can also carry out the experiment in the liquid phase. In that case, bromine water is added drop by drop to chlorine water. The brown drops, as they become diluted, turn canary yellow. Gaseous bromine monochloride is formed and dissolves readily in water, producing a yellow disinfecting liquid, but one that remains dangerous.

Br_2 + SO_2

- The reaction between bromine and sulfur dioxide may be carried out in the gaseous phase using a three-necked flask, but it is perhaps more visible if performed in the liquid phase. To do this, one or two drops of bromine are added to an aqueous solution of sulfur dioxide, that is, sulfurous acid, H_2SO_3. The bromine disappears immediately as its color is discharged. Sulfuric acid and hydrobromic acid have been formed.

Br_2 + NH_3

- The reaction may be carried out in the liquid phase, although this version requires a certain degree of dexterity. Bromine water is poured into a long test tube until it reaches approximately one-eighth of the tube's height. The tube is then rapidly filled with dilute ammonia solution, closed with a finger, and inverted over a water trough. The red color of the bromine disappears, and bubbles are evolved (Figure 68).

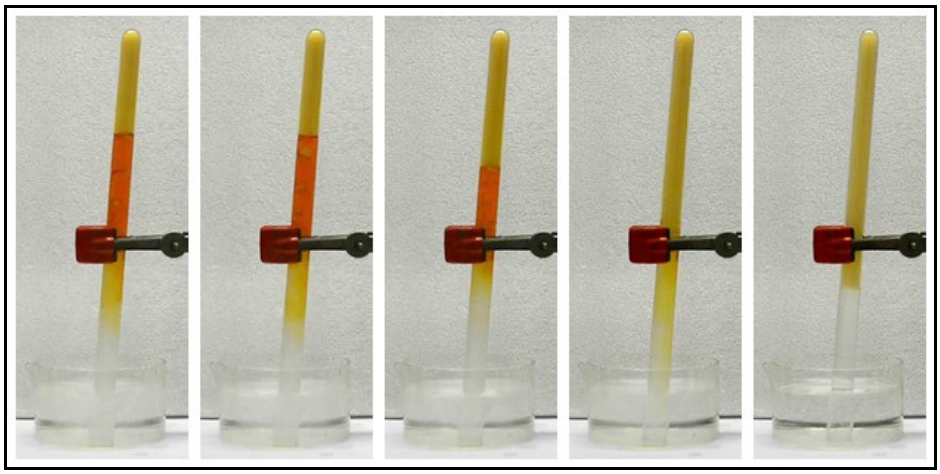


Figure 68

- In a large 2-liter Erlenmeyer flask, red bromine vapor is introduced and the flask is then closed with a two-hole stopper. Through one of the openings, ammonia gas is admitted by means of a tube reaching close to the bottom of the vessel. Since ammonia is much lighter than air, it would otherwise have difficulty reaching the lower part of the flask. A dense white cloud of ammonium bromide forms immediately. The experiment is highly spectacular yet presents little danger.

- Another method consists in allowing a small quantity of liquid bromine to flow into a three-necked flask while ammonia gas is passed continuously through it. A dropping funnel is convenient for this purpose. The white cloud of ammonium bromide is then even denser and leaves through the third neck, from which it may be collected as a white powder in a well-cooled receiving flask. The powder dissolves readily in water.

- A third procedure consists in bringing gaseous ammonia and gaseous bromine together in the same flask. The bromine vapor may conveniently be produced by

passing a stream of air through a flask containing liquid bromine. Although air is introduced in this way, it does not interfere with the reaction.

Br_2 + C_2H_2

- To combine acetylene and bromine safely and without difficulty, acetylene should be bubbled directly through bromine water, or through a small quantity of bromine covered by a layer of water. The liquid becomes decolorized and a complex oily substance is formed.

HBr + Cl_2

- The reaction between chlorine and hydrobromic acid is not easy to carry out entirely in the gaseous phase. It is therefore preferable to perform it using at least one aqueous solution of these two substances. See Chapter 9.3 for further details.

HBr + NH_3

- The preceding experiment may be repeated with essentially the same result by using ammonia and hydrobromic acid instead.

Cl_2 + H_2

- The reaction between chlorine and hydrogen is explosive whenever both gases are present in the gaseous state, except under very dim illumination. The following procedure allows the experiment to be carried out while minimizing the risks involved.

Using salt water, which dissolves only a small amount of chlorine, hydrogen is introduced into a long test tube standing inverted over a trough until approximately one-third of its volume has been filled. From this point onward, the experiment should be conducted under lighting as weak as possible. An opaque tube or cover is placed over the test tube, after which an equal volume of chlorine is introduced.

The apparatus is then taken into direct sunlight and the opaque cover is removed with a quick movement. If the sunlight is sufficiently intense, a violent explosion occurs immediately. The test tube may be thrown out of the trough and great care must therefore be taken never to stand in its likely path.The plastic trough that I used was shattered by the shock. For this reason, I recommend using a metal trough instead. Maximum safety is obtained by placing the entire trough-and-test-tube assembly in a very dark place in a garden and illuminating the test tube from a distance by means of a mirror reflecting sunlight onto it.

IMPORTANT NOTE: Unfortunately, this is one of those experiments described in many chemistry manuals without sufficient emphasis being placed on its hazards and on the absolutely essential precautions that must accompany it.

Cl_2 + NO

- Dry nitric oxide is introduced through one neck of a four-necked flask. Once the orange coloration produced by contact with air has disappeared, dry chlorine is admitted through a second neck. The third neck serves as an outlet for excess gases.

A yellowish nitrosyl chloride, NOCl, is formed. Through the fourth neck, fitted with a dropping funnel, a small quantity of water is then introduced while the flow of both gases is maintained. The water becomes warm and bubbles appear within it. Hydrochloric acid and nitrous acid, HNO_2, are formed. Both acids may be detected by pH measurement, while the presence of hydrochloric acid may be confirmed by means of silver nitrate.

Cl_2 + H_2S

- A large three-necked flask is placed on a magnetic stirrer. Ordinary water, colored orange with a Congo red solution, is poured into the flask to a depth of about 3 cm. Hydrogen sulfide is bubbled into the liquid through one tube and chlorine through another. Hydrogen sulfide should be admitted first, since chlorine alone might destroy the original color of the indicator. The two gases rapidly combine to form hydrochloric acid. The red indicator turns blue. If chlorine is present in excess, the blue coloration is eventually discharged. A layer of sulfur is deposited on the walls of the flask.

NOTE: Such sulfur deposits may readily be removed by means of a solution of ammonium polysulfide.

Cl_2 + SO_2

-A three-necked flask is filled to about one-third of its volume with water. Using bent glass tubes, chlorine is introduced through the first neck and sulfur dioxide through the second, so that the two gases meet beneath the surface of the water. A magnetic stirrer may also be used to facilitate their interaction within the aqueous vortex. The third neck serves as an outlet. To regulate the flow of gases more easily, chlorine may be generated in the liquid phase by reacting hydrochloric acid with sodium hypochlorite solution (bleach). A magnetic stirrer can then be used to control the rate of gas evolution. The liquid in the flask becomes warm and white fumes appear. The liquid is then tested separately with barium chloride and silver nitrate. Both reagents produce precipitates, showing that hydrochloric acid and sulfuric acid have been formed.

The same reaction may be demonstrated more simply by bubbling chlorine through an aqueous solution of sulfur dioxide (sulfurous acid), which also becomes warm.

Another variation may be carried out in a three-necked flask immersed in an ice-water bath and illuminated with ultraviolet light. Five grams of camphor are placed in the flask. Through the first neck, sulfur dioxide previously dried by passage through concentrated sulfuric acid is introduced. The camphor gradually liquefies. Dry chlorine, also passed beforehand through a sulfuric acid drying flask, is then introduced through the second neck. From this point onward, both gases must be admitted slowly and in approximately equal proportions. The quantity of liquid in the flask gradually increases. Sulfuryl chloride, SO_2Cl_2 , is formed. In this state, however, it is contaminated with camphor. When cautiously poured into water, sulfuryl chloride reacts vigorously to produce hydrochloric acid and sulfuric acid, both of which may readily be identified.

$Cl_2 + C_2H_2$

The reaction between chlorine and acetylene is explosive, but several methods make it possible to demonstrate the combination safely.

- One method uses a strong cylindrical vessel with a wide opening, such as a large footed test tube, at least 4 cm in diameter. Water is poured into the vessel to a depth of about 20 to 25 cm. A tube connected to a chlorine generator is immersed in the water. Chlorine production is adjusted so that a steady but not excessive stream of gas is obtained. As soon as the characteristic greenish-yellow chlorine reaches the end of the delivery tube beneath the water, a piece of calcium carbide no larger than a hazelnut is dropped into the vessel. A slight explosion may occur initially. Thereafter, because chlorine and acetylene are continuously supplied at moderate rates, numerous sparks or small flames may be observed in the water or at its surface. When the chlorine generator is stopped and the gas flow decreases, the flames may be seen directly at the opening of the glass tube. Carbon gradually forms and floats on the surface. At certain moments, a fairly large flame may suddenly appear and illuminate the entire apparatus (Figure 69).

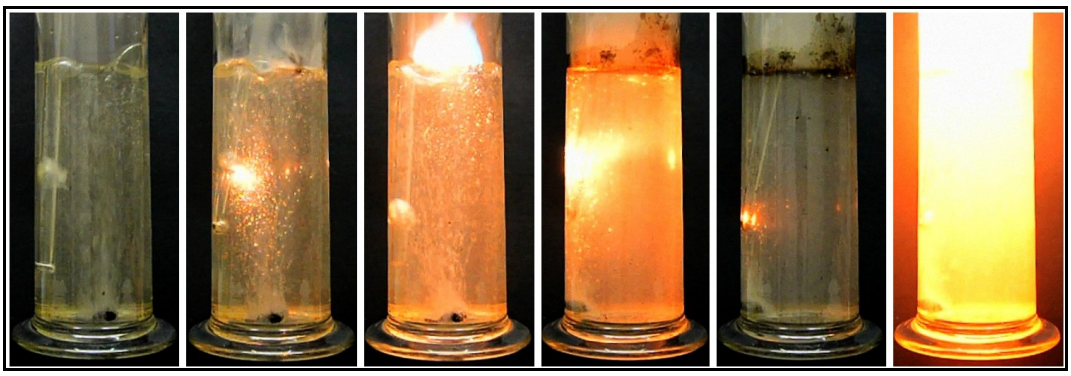


Figure 69

- Another method consists in bubbling acetylene through chlorine water. The effect is less spectacular because no flames are produced, but abundant carbon is formed while hydrochloric acid accumulates in the solution.

- A variation of this procedure consists simply in dropping a piece of calcium carbide directly into chlorine water.

- Another striking yet safe demonstration consists in throwing a piece of filter paper soaked with chlorine water into a flask previously filled with acetylene. The paper ignites immediately, while the walls of the flask become coated with carbon.

- Finally, another attractive and safe method may be used. A tall 1-liter beaker is ideal, although an inverted bell jar or a bell-shaped reactor may also be employed. Three to four centimeters of bleach are poured into the vessel. A piece of calcium carbide is then dropped into the center if possible. Acetylene begins to evolve immediately. Using a PVC pipette, jets of hydrochloric acid are directed into the vessel so that the reaction between the acid and the bleach generates chlorine. Each

addition produces flames while carbon is simultaneously deposited on the walls of the vessel.

Cl_2 + CH_4

-A test tube filled with salt water is inverted over a trough containing the same solution, which dissolves only a very small amount of chlorine. Chlorine is first introduced from below until it occupies approximately one-third of the tube. A second third is then filled with methane, which may conveniently be obtained directly from the natural-gas supply serving the laboratory. The trough and test tube are then exposed to direct sunlight or placed under an ultraviolet lamp. The two gases gradually combine, and the water level rises in the test tube.

HCl + NO_2

A three-necked flask or a suitable reactor is used. Hydrogen chloride and nitrogen dioxide are introduced simultaneously. The hydrogen chloride may be prepared by the action of sulfuric acid on moistened sodium chloride, while the nitrogen dioxide is generated by the action of the same acid on sodium nitrite. The two gases mix in the flask which, if nitrogen dioxide is present in excess—a situation that should be avoided—takes on a red coloration.The gases are then directed into a Drechsel bottle containing potassium bromide or, preferably, potassium iodide. The liberation of bromine or iodine demonstrates that chlorine has been formed.

8.3 With at Least SO_2

- The following experiment theoretically requires only sulfur dioxide. In practice, however, a small amount of air is also involved. A silica tube—not glass of any kind—is placed at an angle of approximately 45° in front of an ultraviolet lamp. Sulfur dioxide is introduced through the lower end of the tube. Being heavier than air, it gradually displaces the air initially present. Both ends of the tube are then closed and the ultraviolet lamp switched on. Depending on the amount of oxygen remaining in the tube, either sulfur gradually deposits on the walls or a white mist of sulfur trioxide appears.

- Another experiment consists in introducing sulfur dioxide and hydrogen sulfide simultaneously into a large three-necked flask. A layer of sulfur forms on the walls while water is produced. Figure 70 shows the appearance of the flask at the end of the reaction. The reaction occurs only in the presence of traces of moisture. It is therefore preferable to place a few drops of water in the flask beforehand rather than bubble the gases through water, in which both are partially soluble. The experiment may also be performed very visibly by using aqueous solutions or, better still, alcoholic solutions of the two gases.

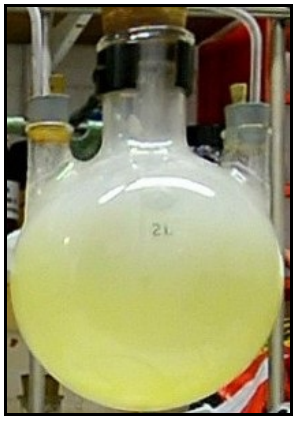


Figure 70

- The following experiment is a classic of inorganic chemistry. It requires a certain degree of dexterity, and the assistance of a second person may even prove useful.
A flask of at least 2.5 liters with a very wide neck, or alternatively a 2-liter flask fitted with three or five necks, is required. Prepare perforated stoppers carrying four glass tubes. Three of these should terminate approximately in the middle of the flask, while the fourth should extend considerably lower. The first tube is connected to a sulfur dioxide generator, for example sodium sulfite and sulfuric acid. The second is connected to a nitric oxide generator, such as copper and nitric acid. The third is connected either to a non-return rubber bulb allowing the operator to blow in air or, preferably, to a small air pump of the type used to aerate aquariums, fitted with a foot switch. The fourth tube, extending lower than the others, serves simply as a gas outlet. Before beginning the experiment itself, pour a small quantity of water into the bottom of the flask and warm it gently. Care should be taken that the lower opening of the gas outlet tube remains well above the water level. Nitric oxide is first introduced into the flask. On coming into contact with the air already present, it develops a reddish coloration. Sulfur dioxide is then admitted. The atmosphere inside the flask becomes colorless once again. At this point, ordinary air is blown into the flask, causing the interior to become red once more. Additional air is introduced whenever necessary so that the flask alternately reddens and becomes colorless. Under these conditions, white crystals gradually begin to form on the walls of the flask. These are the famous lead-chamber crystals, composed of nitrosyl hydrogen sulfate $NOHSO_4$, also known as nitrosylsulfuric acid, once encountered in the industrial manufacture of sulfuric acid. Throughout the experiment, the flask becomes noticeably warm. When a sufficient quantity of crystals has accumulated, the gas generators and connecting tubes are disconnected. The crystals are then washed from the walls by bringing them into contact with water while gently swirling the flask. A fresh evolution of nitrogen dioxide occurs and the flask again develops a red coloration. Once all the crystals have been removed from the walls in this manner, the liquid is poured into a bottle. Its pH is measured with indicator paper, after which barium chloride is added. The solution proves to be strongly acidic, and a precipitate of barium sulfate is formed. These observations show that sulfuric acid has been produced and dissolved in the water.
Since the experiment requires both sulfur dioxide and nitric oxide generators capable of supplying gas continuously for several minutes, suitable quantities of reagents and appropriately sized apparatus must be provided.
This experiment demonstrates on a small scale what takes place on a much larger scale in sulfuric acid plants, where one of the most important chemicals of modern industry is produced. Although the experiment is described in all good chemistry textbooks, it is seldom demonstrated before students because of the skill required to regulate the flow of the various gases involved. Some authors further complicate the apparatus by adding a fifth tube through which steam is introduced. The steam then replaces the water initially present in the flask. Its purpose is to wash the walls periodically so that a greater quantity of sulfuric acid accumulates at the bottom of the vessel. Since the experiment is already sufficiently complex without this refinement, such an addition is of doubtful value and is, in any case, entirely unnecessary from a demonstrational and educational standpoint.

- Take a dry three-neck flask. Through two of the necks insert tubes extending almost to the bottom of the flask. The third neck is fitted with an outlet tube leading outside. Through the first tube introduce sulfur dioxide and, through the second, nitrogen dioxide obtained by the reaction between sodium nitrite and sulfuric acid. The inside of the flask gradually becomes coated with a fine powder. Make sure that the internal diameter of the gas inlet tubes is sufficiently large to prevent clogging. Placing the flask in a cold bath is useful because it favors crystal formation inside the flask rather than in the tubes. Stop the experiment once enough white crystals have been collected. Only a small quantity is needed for the experiment to be successful. Disconnect the apparatus and, while tilting it, allow the remaining dense reddish gas to escape from the three-neck flask. Then add a little water. Effervescence occurs and reddish vapors are again produced. Test the resulting liquid with barium chloride solution. A white precipitate forms because the liquid contains sulfuric acid. This is, again in simplified form, the experimental basis of sulfuric acid manufacture.

8.4 With at Least Ammonia

-A glass tube approximately one meter long and at least 3 cm in diameter is mounted vertically on a stand using a suitable clamp. At the upper end, a plug of cotton or filter paper soaked in ammonia solution is inserted and the tube is closed with a stopper. At the lower end, a similar plug soaked in hydrochloric acid is placed and the tube is likewise stoppered. For some time, nothing appears to happen because hydrogen chloride is a heavy gas whereas ammonia is much lighter. If, however, the outside of the tube is cooled with ice, convection currents develop within it. These currents mix the two gases, which react together and arrest their motion in the form of white streaks of ammonium chloride (Figure 71).
The experiment may also be performed with the tube held horizontally. Before beginning, a strip of moist indicator paper is placed along its entire length. The color changes make it possible to follow the movement of the two gases, ammonia generally advancing more rapidly.
A third variation consists in beginning with the tube arranged vertically as described above and then suddenly inverting it so that the ammonia source is at the bottom and the hydrochloric acid source at the top. In this case, the two gases meet rapidly and produce a conspicuous white cloud that appears to fall from the top of the tube.

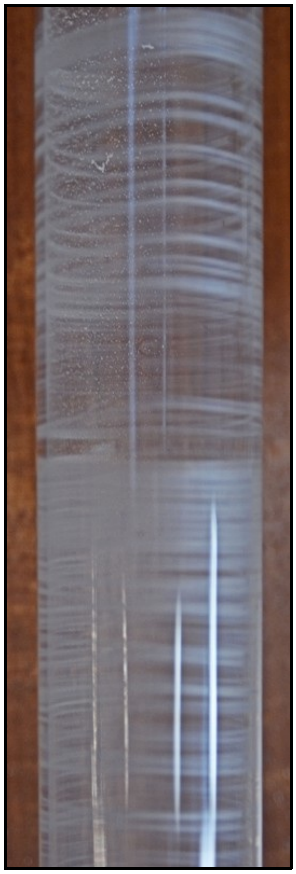


Figure 71

- Another way to do this experiment : under a tightly sealed glass bell jar, place two small beakers, one containing concentrated hydrochloric acid and the other concentrated aqueous ammonia. After one hour, the beaker containing the acid will

have a layer of white powder covering its bottom. The same white powder will also have been deposited on the surface upon which the bell jar rests.

- Carbon dioxide, previously washed through water and then dried in a calcium chloride column, is introduced through one neck of a three-necked flask. Through the opposite neck, thoroughly dried ammonia is admitted after passage through a column containing quicklime. The third neck is closed by a stopper carrying a gas outlet tube for the escape of excess gases. This tube should have an internal diameter of at least 8 mm, otherwise it may become blocked. The meeting of the two gases rapidly produces a white smoke consisting of a fine powder that gradually deposits on the walls of the flask and in the outlet tube. When the flask has become opaque owing to the accumulation of this material, the experiment is stopped and the gas generators disconnected. Two or three milliliters of water are then introduced into the flask, which is gently rotated so that the liquid wets the walls. An immediate cooling effect is observed. Ammonium bicarbonate has been formed. This substance is used in the baking industry as a leavening agent and produces a strongly alkaline solution when dissolved in water.
NOTE: For best results, the amount of carbon dioxide entering the flask should be approximately half that of the ammonia.

-Another experiment involves the reaction between sulfur dioxide and ammonia, both of which must first be thoroughly dried. Sulfur dioxide is dried by passage through a calcium chloride column, while ammonia is dried by passage through a column containing quicklime. For this experiment, I used a reactor fitted with a dome carrying four outlets, three ground-glass joints and one threaded opening. A thermometer was inserted through the threaded opening. Gas inlet tubes were fitted into two of the ground-glass joints, while the third served as the outlet and was connected to a discharge tube. The reactor was immersed in a cooling bath consisting of a stainless-steel container filled with water and refrigerated blocks that had been kept in a freezer for twenty-four hours (Figure 72).

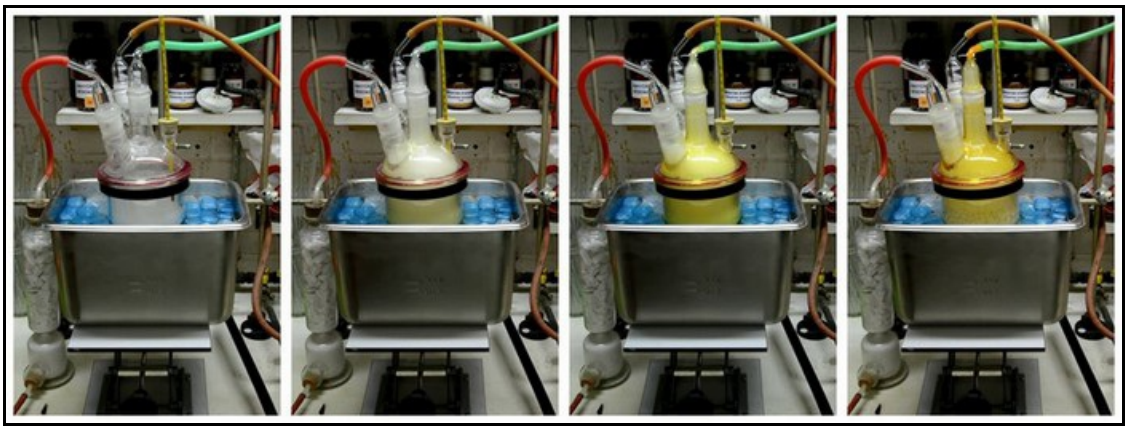


Figure 72

The sulfur dioxide generator is started first and the reactor is filled with this gas. It is important to prevent air from becoming mixed with the reaction gases. The

ammonia generator is then started, the quicklime column purged of air, and finally connected to the reactor. A white cloud appears immediately within the reactor. This rapidly becomes yellow, while a red-orange substance is deposited on the walls and in the discharge tube leading to the outside (Figure 73).

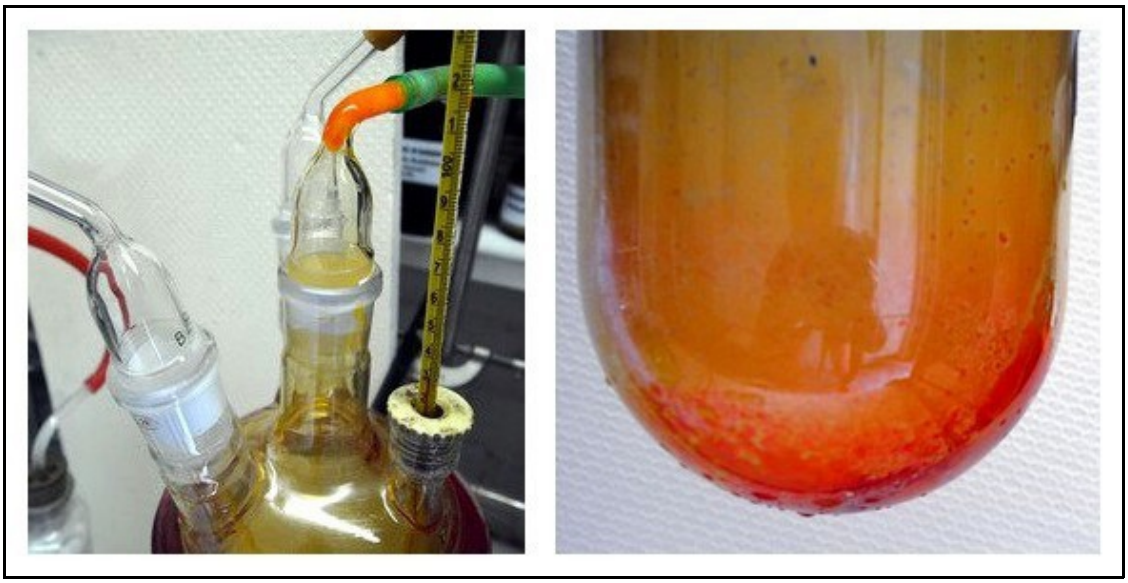


Figure 73

Care must be taken to ensure that the outlet tube does not become blocked. A tube of sufficiently large diameter should therefore be used. The temperature inside the reactor rises by approximately twenty degrees Celsius or more. After some time, the reaction is stopped by disconnecting the ammonia generator. Sulfur dioxide is then allowed once again to fill the reactor, after which the apparatus is left to cool slightly before being opened. The room should be thoroughly ventilated, and the ammonia generator removed beforehand.

The composition of the products obtained, whether white, yellow, or red-orange, varies according to the relative proportions of the reacting gases at any given moment. In general, the products consist of a mixture of amidosulfurous acid and ammonium amidosulfite. If the reactor were not immersed in the cooling bath, the walls would become much hotter and the solid products would be deposited much farther along the outlet tube, a situation that should obviously be avoided. The products are dissolved together in distilled water and collected as a single solution. This aqueous solution exhibits the following reactions:

a) With hydrogen peroxide, oxygen is evolved.
b) With hydrochloric acid, a fleeting pink coloration appears.
c) With nitric acid, reddish-brown fumes are evolved and colloidal sulfur is formed.
d) A green nickel sulfate solution turns blue.
e) An orange potassium dichromate solution becomes canary yellow.
f) A copper sulfate solution gives a precipitate of dull yellow-green color.
g) A ferric chloride solution gives an orange-brick precipitate.
h) A pink manganese chloride solution gives a white precipitate.
i) A lead acetate solution gives a white precipitate.

j) A mercuric nitrate solution gives a gray precipitate.
k) A sulfuric solution of cerium sulfate gives a white precipitate.
l) A barium chloride solution gives a white precipitate.
m) A potassium permanganate solution is decolorized.

- Hydrogen sulfide and ammonia, both carefully dried beforehand, may be brought together in a three-necked flask immersed in a freezing mixture of ice and salt. As the two gases mix, a thin white deposit forms on the walls of the flask. Its composition varies according to which gas is present in excess. If a slight amount of moisture is present either in the flask or in the gases, the deposit acquires a yellowish-green tint.
The reaction may also be carried out by first dissolving ammonia in ethyl alcohol and then bubbling hydrogen sulfide through the solution. Crystals of ammonium hydrosulfide are then deposited on the walls of the vessel

8.5 With NO or NO_2

- A gas bulb fitted with a stopcock at each end is partially filled with nitric oxide. On coming into contact with the air initially present in the bulb, the gas produces a red mixture. Both stopcocks are then closed and the bulb is placed in a freezer. After a few minutes, the red color becomes noticeably less intense. Simply holding the bulb in one's hand, however, causes the red coloration to return. This occurs because the relative proportions of the colorless and colored species present in the mixture depend upon temperature.

- other experiment may be performed in a three-necked flask or a suitable reactor. Hydrogen chloride and nitrogen dioxide are introduced simultaneously. The hydrogen chloride may be prepared by the action of sulfuric acid on moistened sodium chloride, while the nitrogen dioxide is generated by the action of the same acid on sodium nitrite. The gases mix within the flask, which becomes red if nitrogen dioxide is present in excess, a condition that should be avoided whenever possible. The gaseous mixture is then passed into a Drechsel bottle containing potassium bromide or, preferably, potassium iodide. The liberation of bromine or iodine demonstrates that chlorine has been formed.

- Hydrogen sulfide and nitrogen dioxide may be brought together in a three-necked flask, or in a large flask fitted with a three-hole stopper. The walls of the vessel rapidly become coated with sulfur while droplets of water appear at the end of the outlet tube, especially if this tube is cooled. The reaction produces sulfur, water, and nitric oxide. The latter is difficult to identify directly, even if a large flask is inserted before the outlet tube in the hope of observing the re-formation of nitrous fumes upon contact with air. In practice, such observations are difficult because the additional flask also rapidly becomes opaque owing to the deposition of sulfur on its walls.

Chapter 9 - Reactions Between a Gas and a Liquid or a Liquid Containing Solid Particles

VARIOUS GASEOUS SOLUTIONS

In many cases, bubbling a gas through a liquid may be replaced by allowing that liquid to react with an aqueous solution of the gas. This is true, for example, of HBr, HI, Br_2, Cl_2 , SO_2 and H_2S.

The preparation of hydrobromic acid and hydriodic acid solutions has already been described earlier.

Bromine water is very easy to prepare. Place a small quantity of bromine in a well-sealed amber bottle and add a considerably larger volume of water. Shake and allow the mixture to stand. Prolonged contact between the two phases is recommended.

To prepare chlorine water, pass chlorine gas into previously boiled water contained in a flask immersed in an ice-water bath until saturation is reached. Stopper the flask tightly and store it in a cool, dark place. Chlorine water can be kept for several months under these conditions. If a portion must be withdrawn while the remainder is to be preserved, it is prudent to flush the bottle with carbon dioxide (or, preferably, argon) before resealing it.

Solutions of H_2S and SO_2 may be prepared in the same manner. The aqueous solution of SO_2 is generally regarded as a dilute solution of sulfurous acid and keeps reasonably well when protected from air. An aqueous solution of H_2S, however, unfortunately has only a limited shelf life.

9.1 Air or Oxygen

The following experiment is difficult to place in any single category. Small pieces of yellow phosphorus are placed in a 100 mL ground-glass flask containing enough

water to fill approximately one quarter of the bulb. A long, wide, highly transparent vertical glass tube is inserted into the neck, and the flask is heated in as complete darkness as possible. As soon as the water begins to warm, and for a relatively short period, tiny luminous points can be seen flashing briefly within the liquid. This phenomenon is caused by phosphorus reacting with the oxygen dissolved in the water. It ceases once that oxygen has been consumed. As the temperature continues to rise, the water eventually reaches boiling. Throughout this process, and especially once boiling begins, extremely fine particles of phosphorus are carried upward by the steam into the glass tube, where they become phosphorescent. One then observes what resembles a pale green flame fluctuating under the influence of the air currents generated within the tube by the continuous evaporation and condensation of water vapor (Figure 74).

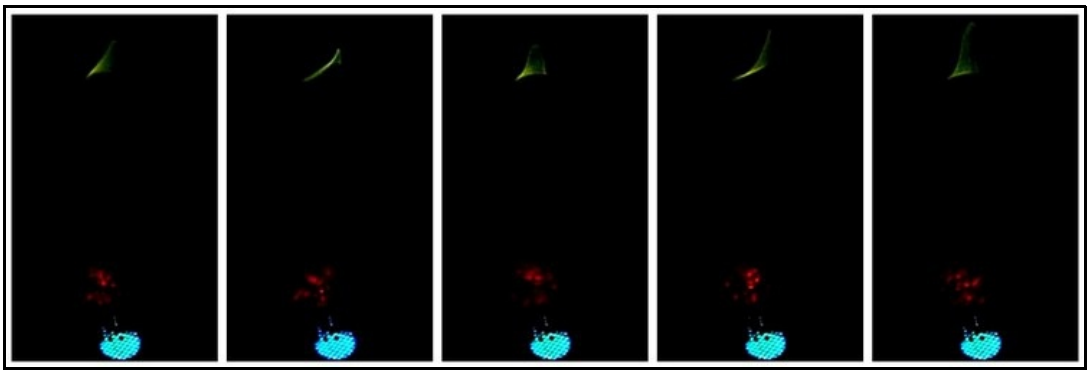


Figure 74

- To demonstrate that air always contains a small amount of carbon dioxide, air from a small compressor is bubbled through baryta water. The characteristic precipitate of barium carbonate appears rather quickly. A similar reaction occurs with limewater, although much more slowly because limewater is less sensitive.

- A Kjeldahl flask is preferred to an ordinary flask because its long, narrow neck and constricted upper portion reduce splashing. Powdered antimony is placed in the flask and covered with water to nearly half its height. A wide tube is introduced through the neck so that a strong stream of air can later be blown through the liquid. The water is brought to a boil and the air pump started. Steam is initially produced, but this soon ceases because the incoming air cools the liquid to a temperature well below its boiling point. The pump is stopped, boiling is allowed to resume, and the pump is restarted. This cycle is repeated at least ten times. Gradually the liquid becomes cloudy and gray as antimony oxide forms. Not all of the antimony can be converted by this method, but a significant quantity of oxide can nevertheless be produced. It may be recovered as a white powder by simple decantation and drying. The oxide reacts readily with hydrochloric acid.

- A small amount of barium chloride is dissolved in freshly prepared sulfurous acid obtained by bubbling SO_2 through previously boiled water that has been allowed to cool in a completely filled and tightly stoppered bottle. Nothing noteworthy occurs. If a strong stream of air is then passed through the liquid, a white precipitate

appears as sulfurous acid is gradually converted into sulfuric acid. If the experiment is continued long enough, the characteristic odor of SO_2 and sulfurous acid disappears completely, together with their bleaching properties. The sulfuric acid produced remains relatively dilute, however.

- A slightly different experiment gives the same result. If a little chlorine water is added to the clear mixture of fresh sulfurous acid and barium chloride, a white precipitate of barium sulfate forms immediately. Chlorine water is likewise capable of oxidizing sulfurous acid into sulfuric acid.

- Pour a small quantity of aqueous sodium sulfide solution into a beaker. Place the beaker in the open air beneath a glass bell jar supported on two bricks. The purpose is to allow free circulation of air while preventing foreign matter from falling into the liquid. After standing overnight, the solution will have been transformed, at least partially, into sodium thiosulfate, as shown by its ability to decolorize an iodine solution. A comparable result can be obtained more rapidly by using a pump to pass a prolonged stream of air through the sodium sulfide solution.

- Place a substantial quantity of concentrated ammonia solution in a wash bottle and immediately pass a strong stream of air through it. The temperature gradually falls until condensation appears on the outside of the bottle. In some cases, a small quantity of water placed between the wash bottle and a thin metal sheet may even freeze.

- Several centimeters of carbon disulfide are placed in a 500 mL pear-shaped flask. Through a three-hole stopper, a glass tube reaching nearly to the bottom of the flask delivers a strong stream of air from a compressor, the flow being regulated by a three-way stopcock. A thermometer capable of reading down to -20 °C passes through the second opening. The third opening is connected to an appropriate exhaust system, since carbon disulfide vapors are both highly flammable and toxic. No flames should be present either in the laboratory or near the exhaust outlet. A considerable decrease in temperature is rapidly observed.

- Copper turnings are placed in a pear-shaped flask together with hydrochloric acid. A strong stream of air is introduced through the bottom of the apparatus, while the gaseous vapors are immediately vented outdoors from the top. The liquid soon acquires a yellow coloration owing to the formation of $CuCl_2$, which is yellow in concentrated hydrochloric acid. After several minutes, the yellow solution is collected. A small portion is boiled until only a dense drop remains. Ammonia solution is then added. A beautiful blue liquid is obtained.

- Pass gaseous or liquid hydrochloric acid into a blue copper sulfate solution until the blue copper chloride solution has been converted into the green copper chloride solution. Place this liquid in a Drechsel bottle and then pass a stream of very hot air through it. To do this, use a pump and a refractory tube heated to a very high temperature. Keep the connection between the outlet of this tube and the Drechsel

bottle as short as possible, and preferably use silicone or rubber tubing, but not PVC. Connect a second Drechsel bottle to the outlet of the first one, containing a sodium hyposulfite (thiosulfate) solution. It will gradually become milky owing to the formation of sulfur produced by chlorine. In fact, the oxygen in the air combines with the green chloride to regenerate the blue chloride and water while releasing chlorine, which causes sulfur to precipitate in the sodium hyposulfite solution.

- A 200 mL flask is filled with water to well above its midpoint, and a few small pieces of yellow phosphorus are introduced. The flask is heated until the phosphorus melts. A stream of air—or, better still, oxygen—is then directed through a swan-neck tube so that it emerges close to the phosphorus. The phosphorus reacts vigorously, particularly in pure oxygen. Brief flashes of flame can be seen. Although spectacular, the experiment is safe provided that the layer of water above the phosphorus is sufficiently deep (Figure 75).

Figure 75

- A solution of ferrous chloride or ferrous sulfate is treated with sodium hydroxide solution, producing a greenish-white precipitate. If air is bubbled through the mixture, the precipitate gradually turns reddish.
If, however, air had first been bubbled through the ferrous solution before the addition of sodium hydroxide, the solution would have become yellowish and the precipitate subsequently obtained would have been reddish-brown from the outset.

- Air is bubbled for an extended period through a concentrated aqueous solution of phenol to which a small quantity of ammonia has been added. Very slowly, the liquid develops a blue coloration. In some cases, it is necessary to allow the solution to stand overnight before the color becomes fully apparent. The beautiful blue color is caused by the formation of phenocyanin. Exposure to sunlight intensifies the coloration. If sodium hydroxide solution is added, the blue color disappears within about twenty-four hours. Boiling appears to accelerate this fading process. Conversely, adding hydrogen peroxide to the blue solution causes it to become yellow after approximately twenty-four hours.

- A colorless aqueous solution of pyrogallic acid is prepared and pure oxygen is bubbled through it. The solution becomes brown. If a small quantity of alkali had been added beforehand, the color would have turned distinctly black. The same reaction occurs with air, although somewhat more slowly.
This reaction was once recommended as the basis of a simplified analysis of atmospheric air. The experiment may be performed in a long, stoppered test tube partially filled with pyrogallic acid solution and, if possible, placed for an extended period on a mechanical shaker. At the end of the experiment, the tube is opened under water while being held vertically. The rise of water inside the tube allows the volume of oxygen that has reacted to be measured.

-A simple variation may also be performed. Two small beakers are prepared, each containing a small quantity of pyrogallic acid. Water is added to the first beaker and the mixture stirred. Nothing remarkable occurs immediately, but the liquid gradually turns brown. The same quantity of water is added to the second beaker, followed immediately by a drop of aqueous potassium hydroxide or sodium hydroxide solution. Again, nothing noticeable happens at first. However, a brief stirring with a glass rod rapidly produces a brown coloration. The presence of alkali greatly accelerates the absorption of oxygen from the air.

- Three Drechsel bottles are arranged in series. The first contains baryta water and is connected to a second containing a solution of tannic acid. This second bottle is connected in turn to a third, which also contains baryta water. Air is passed through the apparatus. The carbon dioxide naturally present in the air reacts in the first bottle to form a slight precipitate. Interestingly, a more abundant precipitate appears in the final bottle, which also contains baryta water. This occurs because the aqueous tannin solution reacts with atmospheric oxygen to produce carbon dioxide and gallic acid. If the experiment were continued long enough, the gallic acid would eventually cloud the tannin solution, which is therefore best prepared relatively dilute.
The experiment becomes even more instructive if two or three baryta-water bottles are placed before the tannin solution. Under those conditions, the second and third baryta-water bottles remain perfectly clear because all of the original atmospheric carbon dioxide has already reacted in the first bottle.

9.2 Hydrogen or Nascent Hydrogen

- There is generally little point in bubbling hydrogen gas through a liquid, since under ordinary circumstances no reaction will occur. It is, however, very common to generate hydrogen directly within a liquid. This particularly reactive form of hydrogen was formerly referred to as nascent hydrogen. The following four experiments provide attractive demonstrations of its reducing action.

- A small ball made from a piece of household aluminum foil is dropped into a

sodium hydroxide or potassium hydroxide solution colored violet with phenolphthalein. Very quickly, complete decolorization occurs. This effect is attributed to nascent hydrogen. The aluminum is then removed with a spatula or lancet, and a small quantity of hydrogen peroxide is added to the liquid. A reddish coloration briefly reappears.

- A little methylene blue powder is added to a sodium hydroxide solution and stirred until the liquid is uniformly colored. A small ball of household aluminum foil is then introduced. Under the influence of nascent hydrogen, the solution gradually becomes colorless. The aluminum is subsequently removed and discarded. Hydrogen peroxide is then added dropwise to the decolorized solution. Each drop temporarily restores the original blue color, although the coloration remains visible only for a short time.

- A dilute aqueous solution of methylene blue is prepared so that the liquid remains perfectly transparent. A piece of zinc is introduced, followed by a few drops of hydrochloric acid. Nascent hydrogen gradually decolorizes the solution. If a few drops of ferric chloride solution are then added, the original blue coloration returns.

- An aqueous solution of permanganate is acidified with sulfuric acid. No visible change occurs. A strip of zinc is then immersed in the liquid. If the contact between the acid and the zinc does not immediately generate nascent hydrogen, additional acid is added. Once hydrogen evolution begins, the mixture is left undisturbed. Gradually, the purple solution turns brown and small black particles of manganese oxide appear.

9.3 HBr, HI, I_2, Br_2 , and Cl_2

- A long test tube is filled with gaseous HBr by downward displacement. A few drops of fuming nitric acid are then introduced. The tube rapidly fills with red bromine vapors.
The same effect is obtained by adding a few drops of nitric acid to a flask containing a small quantity of hydrobromic acid solution.

- Hydrobromic acid (48%) is a heavy liquid. When chlorine water is poured into this acid, an orange color appears, indicating the liberation of bromine. Adding nitric acid also gradually liberates bromine, the flask changing from orange to dark brown. Sulfuric acid acts more rapidly but releases both bromine and sulfur dioxide. Adding hydrogen peroxide to hydrobromic acid also liberates bromine.

- If a few drops of silver nitrate solution are added to hydrobromic acid, a white precipitate forms and immediately disappears. More silver nitrate must be added for the whitish-yellow precipitate to remain.

- As mentioned earlier, the reaction between chlorine and hydrobromic acid is more conveniently carried out when at least one of the reactants is used in aqueous solution. In practice, the simplest method is to bubble chlorine through an aqueous solution of hydrobromic acid. The solution quickly turns yellow and then increasingly deep orange while bromine vapor gradually fills the entire flask before spilling out of it by gravity (Figure 76).

Figure 76

The reaction proceeds equally well when both gases are used in aqueous solution. In that case, the initially almost colorless liquids immediately produce a colored mixture. The liberated bromine can then be readily demonstrated by adding chloroform and shaking.
The reaction between chlorine and hydriodic acid may be carried out in exactly the same two ways.

- A long test tube is filled with gaseous HI by downward displacement, after which a few drops of fuming nitric acid are added. A flame may appear, and the tube invariably becomes filled with iodine crystals.

Figure 77

- A magnetic stirring bar, a small quantity of iodine, and water are placed in a Drechsel bottle. A continuous stream of chlorine is then passed through the mixture while stirring vigorously. The iodine gradually disappears, yielding a colorless solution. Hydrochloric acid and iodic acid are formed. After an excess of chlorine has been introduced, the liquid is transferred to a test tube and concentrated sulfuric acid is added. A large quantity of chlorine is evolved and the liquid turns yellow owing to the formation of iodine pentachloride, ICl_5 (Figure 77).

- Dissolve a small amount of iodine in carbon disulfide and place the solution in a Drechsel bottle whose head has been cooled with an ice pack. Then pass thoroughly dried chlorine through it. The liquid turns brown while becoming warm, and a reddish-yellow oily liquid gradually forms in the head of the Drechsel bottle. This is iodine trichloride (ICl_3) dissolved in carbon disulfide. At the end of the experiment, the odor from the flask is unbearable.

- A highly concentrated bromine water of deep blood-red color is prepared by allowing bromine to remain in contact with water for several days. Immediately before the experiment, the excess liquid bromine is separated from the bromine water, which is then transferred to a thin-walled test tube fitted with a screw cap. The tube is placed in a freezer and carefully monitored so that the entire contents do not solidify. At a certain point, a red mass separates from the liquid and either settles to the bottom or adheres to the walls, while a yellow-orange liquid remains above it. This red material is bromine hydrate (Figure 78).

Figure 78

- A glass rod is dipped into a sodium hydroxide solution and allowed to drain until only a thin film remains. The rod is then exposed to bromine vapors and finally immersed in a test tube containing aniline water. An immediate yellow to orange coloration appears, depending on the amount of sodium hypobromite that has formed.

- Using a small aquarium pump, a stream of air is passed through a flask containing a little bromine so that bromine vapors are carried into a sodium hydroxide solution. A drop of aniline is then added to the solution. A yellow precipitate first appears, then turns red, and finally brown. A simpler procedure consists of introducing bromine vapors into a large flask containing a small quantity of sodium hydroxide solution at the bottom and then shaking the flask.

- Bromine vapors carried by a stream of air are passed through an aqueous solution of sodium thiosulfate. The solution gradually becomes cloudy white and then opaque yellow owing to the formation of a sulfur precipitate. Hydrobromic acid and sulfuric acid are also produced.

- A solution of potassium hydroxide in ethyl alcohol is prepared and placed in a cylindrical vessel standing on a magnetic stirrer. Bromine is added dropwise while the mixture is stirred continuously. The liquid warms noticeably and a white deposit appears. Addition of bromine is continued until the liquid above the deposit becomes yellow. After settling, a yellow liquid with a pleasant odor separates from the white deposit. The deposit itself dissolves in water to produce a yellow solution.

- Bromine is added dropwise to a cooled solution of yellow phosphorus in carbon disulfide while the mixture is stirred magnetically. The liquid gradually becomes cloudy and then clears again. The resulting solution contains phosphorus tribromide dissolved in carbon disulfide. Continued addition of bromine eventually produces phosphorus pentabromide, which precipitates because it is only sparingly soluble in carbon disulfide. Toxic fumes are evolved throughout the process. Adequate ventilation is therefore essential, or the experiment should be carried out outdoors.

- Antimony shot and ether are placed in a double-walled tube cooled by circulating water from a refrigerated reservoir containing ice packs (Figure 79). Pure bromine is then added gradually. A substance that is partly oily and partly solid slowly forms. Upon contact with water, it turns white. This material is a bromoantimonous ester.
Similar bromoferrous and bromoaluminum esters may also be prepared, although my own attempt using aluminum was unsuccessful.

Figure 79

- Bromine vapors carried by a stream of air are passed through a basic solution of fluorescein displaying its characteristic bright yellow-green fluorescence. The solution gradually turns pink as tetrabromofluorescein, better known as eosin, is formed.

- Well-washed chlorine is passed through a Drechsel bottle or U-tube containing liquid bromine. The gas leaving the apparatus is then directed into a strongly cooled spiral condenser. The gas obtained is reddish-yellow, noticeably less red than bromine itself. When collected in water maintained below 10 °C, it produces a yellow solution which reacts with sodium hydroxide to yield a colorless mixture of chloride and bromate. The experiment is somewhat demanding because both the Drechsel bottle and the condenser must be cooled simultaneously. The former is cooled with an ice-water mixture, while the latter requires an ice-salt bath. The bromine chloride

formed begins to decompose already at about 10 °C.

- Chlorine is bubbled through bromine water. The initially reddish liquid eventually becomes yellow. Depending on the experimental conditions, either bromic acid ($HBrO_3$) is formed, or bromine chloride dissolved in water together with a bromate.

- By contrast, when chlorine water is poured into bromine water, one generally obtains only a precipitate of colloidal sulfur.

- Place small pieces of selenium in a Drechsel bottle, moisten them with water, then pass chlorine through the apparatus. A red coloration appears because the black selenium is converted into red selenium. Quickly open the Drechsel bottle, add about 2 cm of water, then continue passing chlorine through it. The selenium pieces gradually disappear because a mixture of selenic acid and hydrochloric acid is formed. Then slowly heat the liquid to remove most of the hydrochloric acid. If a sodium sulfite solution is subsequently added, the liquid gradually turns yellow, then red, and finally deposits red selenium.

If chlorine is bubbled through water cooled to slightly below 0 °C, yellow crystals of chlorine hydrate are formed. This is not a particularly striking demonstration because ordinary ice crystals and chlorine hydrate crystals become intermingled, ultimately producing a compact mass in which only pale yellow-green regions can be distinguished from colorless ones.
The experiment may also be carried out by using a calcium chloride solution instead of distilled water.Pass a large excess of chlorine into a Drechsel bottle placed in a cooling bath and containing a calcium chloride solution. After some time, the liquid becomes filled with small crystals which settle to the bottom, unlike ice crystals, which would float. These are chlorine hydrate crystals (Figure 80).
Conversely, if chlorine water is exposed to sunlight, oxygen bubbles are evolved and hydrochloric acid is formed.

Figure 80

- If chlorine is bubbled through an aqueous solution of hydrogen sulfide, or if hydrogen sulfide is bubbled through chlorine water, a precipitate of colloidal sulfur is obtained, easily recognized by its milky appearance.

- If chlorine is bubbled through an aqueous sodium sulfide solution, a small amount of sulfur first appears at the surface. After prolonged treatment, the solution suddenly loses its clarity and becomes distinctly milky owing to the formation of a

much larger quantity of sulfur.

- Whereas the action of chlorine on bromine and iodine presents little danger, its reaction with ammonia is potentially hazardous because highly unstable and explosive nitrogen trichloride may be formed under certain conditions. To prevent this, ammonia must always be maintained in large excess. Ideally, chlorine is therefore bubbled slowly into at least 100–200 mL of highly concentrated ammonia solution. Thick white clouds of ammonium chloride immediately appear. The experiment should be stopped after only a short time.
A completely safe alternative consists of placing a glass containing chlorine water near a flask previously filled with concentrated ammonia. A white cloud of ammonium chloride forms at once between the two vessels.
A third method consists of mixing aqueous solutions of the two gases. A very long test tube, preferably no more than 2 cm in diameter, is used. A burette with its stopcock closed may also serve. The tube is filled to nine-tenths of its volume with well-chilled chlorine water. It is then quickly topped up with concentrated ammonia solution and immediately closed with a finger. The tube is inverted into a very small water trough, itself placed within a larger dish intended to collect any overflow. Beforehand, the arrangement should be made so that the inverted tube can be held securely in a clamp. The two solutions soon begin to react, producing numerous small bubbles that collect at the upper end of the tube, which takes on a whitish appearance. These bubbles consist of nitrogen gas, and all danger is thereby avoided (Figure 81).

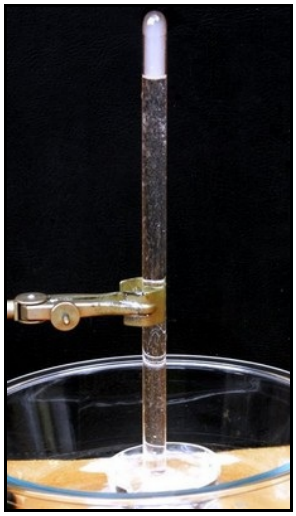


Figure 81

- A few pieces of gold leaf are placed in a flask containing boiled water through which chlorine is bubbled. Before long, the liquid turns yellow and the gold gradually disappears. Various gold salts are formed, including what has been described as chloroauric acid.

- Chlorine is bubbled through a solution of sulfur dioxide. Hydrochloric acid and sulfuric acid are formed and may be identified respectively by silver nitrate and barium chloride. The experiment may also be performed by mixing sulfur dioxide solution (sulfurous acid) with chlorine water.

- Sulfur dioxide and chlorine are simultaneously passed through a flask containing acetic acid. Sulfuryl chloride and monochloroacetic acid, a fuming liquid, are formed. If this liquid is mixed with water, sulfuric acid is produced.

- Chlorine is bubbled through hydrogen peroxide. A vigorous evolution of oxygen occurs. This may be confirmed by placing a glowing splint at the outlet of the apparatus; the splint immediately reignites. Measurement of the final pH shows that the liquid has become strongly acidic owing to the formation of hydrochloric acid.

- Chlorine, previously washed with water, is bubbled through a Drechsel bottle containing a mixture of 100-volume hydrogen peroxide and sodium hydroxide solution. In daylight, faint reddish glows soon become visible. In darkness, these are much easier to observe and appear as tiny “flaming bubbles” (Figure 82). This chemiluminescent reaction is the experiment originally described by the French chemist Mallet and is caused by the formation of what is now known as singlet oxygen.
Another, simpler experiment demonstrating the same chemiluminescent phenomenon may be carried out using sodium dichloroisocyanurate, which is used for swimming pool water treatment. Concentrated hydrogen peroxide is added dropwise onto a layer of small granules of this sodium salt. In complete darkness, every contact between the two substances produces a characteristic red glow. The experiment may also be carried out by dropping a piece of this substance into hydrogen peroxide.
WARNING: in the latter case, use a sufficiently large container because a vigorous evolution of chlorine bubbles produces abundant foam. Ensure excellent ventilation.

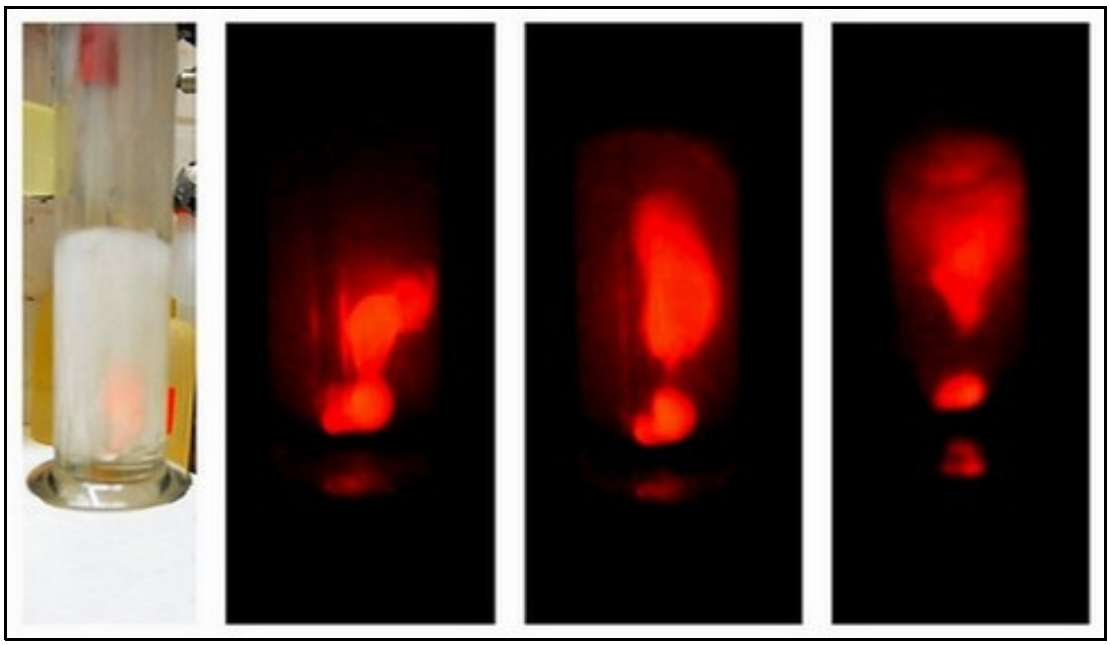


Figure 82

- Chlorine is bubbled through water containing suspended magnesium oxide (or magnesium hydroxide). The liquid acquires a greenish tint as magnesium hypochlorite is formed, a substance possessing strong bleaching properties. This solution cannot be stored for long because it rapidly converts into a mixture of magnesium chloride and magnesium chlorate. If hydrochloric acid is added shortly after preparation, chlorine is liberated once again.

- Barium hydroxide and water are placed in an Erlenmeyer flask standing on a heated magnetic stirrer. The mixture is warmed and stirred from time to time. The suspension remains cloudy. Once the temperature has reached approximately 50–70 °C, chlorine previously freed from hydrochloric acid by passage through

water is introduced. After some time, the mixture appears to become more homogeneous while remaining as white as milk of lime. It then clears rather suddenly. When the liquid has become completely transparent, the chlorine flow is stopped and the solution is allowed to cool. A solution of barium chlorate has thus been prepared. Its presence may be verified as follows. Place 1 mL of aniline and 1 mL of water in a test tube and mix. Add 1 mL of concentrated sulfuric acid. A white precipitate forms. When this reagent is mixed with an aqueous solution of any chlorate, a blue or violet coloration is produced.
If concentrated sulfuric acid is added dropwise to a solution of barium chlorate, a heavy white precipitate of barium sulfate forms together with chloric acid. This acid is unstable and cannot be stored.
WARNING: Barium chlorate should never be isolated as a solid because it is then highly unstable and may ignite or explode upon contact with many substances. Keeping it in solution is possible, although of little practical value. For the amateur experimenter, this experiment remains little more than a laboratory curiosity.

- Chlorine is bubbled through a manganese chloride solution maintained at approximately −5 °C. A yellow to brown precipitate forms, depending on the concentration of the solution. In some cases, the precipitate appears only after chlorine has been passed for quite some time.

- An aqueous solution of manganese sulfate is treated with potassium carbonate solution. A white precipitate of manganese carbonate forms immediately. If left exposed to air, it would gradually turn brown. Instead, the precipitate is allowed to settle briefly, the excess liquid is decanted, and the remaining suspension is transferred to a Drechsel bottle through which chlorine is passed. The color changes progressively, eventually becoming brown and then black. Manganese dioxide has been formed.

- Manganese dioxide is suspended in a moderately concentrated sodium hydroxide solution contained in a vessel heated in a water bath to approximately 35 °C. Chlorine is then bubbled through the mixture. As soon as foaming begins—care being taken not to overfill the vessel—the chlorine supply is stopped and the liquid is filtered or allowed to settle. A characteristic coloration then appears, indicating the formation of purple permanganate.

- Chlorine is bubbled through a concentrated aqueous copper sulfate solution. After a few minutes the operation is stopped. The solution generally appears unchanged. However, if left standing in a closed flask, it gradually develops a deep green coloration, indicating the formation of a concentrated solution of copper(II) chloride. Addition of water restores the familiar blue color.

- Chlorine is bubbled through a moderately concentrated solution of sodium sulfite contained in a Drechsel bottle. Nothing obvious seems to occur, although the liquid becomes noticeably warm. When the experiment is stopped and the apparatus dismantled, the solution is found to have become distinctly acidic. The liquid is

divided into two portions. A few drops of silver nitrate solution are added to the first portion, producing the characteristic precipitate given by chlorides.To demonstrate that this result is not caused by residual chlorine, a small quantity of iron filings is added to the second portion. After a short time, the solution develops a dirty yellow color due to ferrous chloride being oxidized to ferric chloride by atmospheric oxygen. The experiment therefore demonstrates the formation of hydrochloric acid.

- Chlorine is bubbled through a sodium thiosulfate solution. Sulfur precipitates immediately.

- Chlorine is bubbled through a freshly prepared aqueous sodium cyanide solution contained in a Drechsel bottle. The liquid successively becomes yellow, red, and finally increasingly black while warming noticeably. The final product is a heavy, black, viscous liquid consisting of paracyanogen.
WARNING: This material must never be heated. The room should be very well ventilated, and the gases leaving the Drechsel bottle must not be inhaled because of their extreme toxicity. Ideally, the experiment should be carried out outdoors, and the resulting product discarded in a large volume of water.

- Approximately 30 mL of nickel sulfate solution is treated gradually with freshly prepared aqueous sodium cyanide. The precipitate that first appears soon redissolves in an excess of reagent, yielding a solution containing a double nickel–potassium cyanide and displaying a beautiful yellow color. A substantial quantity of chlorine is then bubbled through this solution. At first, the liquid becomes slightly darker. A brown ring subsequently appears around the flask at the surface of the liquid. Finally, the solution loses its transparency completely and a gray precipitate forms.

- Chlorine is bubbled through a concentrated solution of potassium ferrocyanide. The solution changes from yellow to greenish-yellow and then darkens progressively until it appears almost black. Viewed in transmitted light, however, it is seen to be brown. Potassium ferricyanide has been formed. This may be confirmed by its characteristic reaction with ferrous sulfate.
The experiment may also be performed in a very different manner using chlorine water instead of gaseous chlorine. A small quantity of potassium ferrocyanide solution is poured into a test tube to a depth of about 2 cm. A small layer of chlorine water is then carefully added above it. At first, no visible change occurs. The tube is left undisturbed. After several tens of minutes, a blue-green ring appears at the top where the liquid is in contact with the air. When the tube is shaken, this blue-green coloration may spread downward through the liquid. If a large quantity of chlorine water is added at once, the yellow solution turns orange owing to the formation of ferricyanide.

- Chlorine is bubbled through a dilute boiling solution of potassium ferricyanide. A green precipitate forms which, after settling and decantation, leaves a green solution of complex composition.

- Chlorine is bubbled through a potassium iodide solution. Depending on the concentration of KI and on the rate at which chlorine is introduced, several color changes may be observed successively, including green, yellow, and finally black. Once the liquid becomes black, iodine precipitates. Continued introduction of chlorine then attacks the iodine, gradually producing a yellow solution containing a combination of iodine trichloride and potassium chloride.

- A precipitate of lead carbonate is prepared by mixing lead acetate solution with sodium carbonate solution. Chlorine is then bubbled through the suspension. The liquid acquires a reddish-brown coloration.

- A white precipitate of lead chloride is prepared by mixing solutions of lead acetate and hydrochloric acid. The precipitate is then washed thoroughly. Several experiments may subsequently be performed:
a) A portion of the precipitate is dissolved in concentrated hydrochloric acid and chlorine is bubbled through the solution. A yellow solution of lead tetrachloride, $PbCl_4$, is obtained.
b) The precipitate is suspended in a saturated sodium chloride solution and chlorine is bubbled through the mixture. A yellow solution containing a double chloride of composition $PbCl_4$ + NaCl is formed. This liquid attacks various metals such as aluminum and iron, decolorizes indigo, and reacts with alkaline sulfides.
When an excess of reagent is present, the solution becomes brownish. Addition of sodium hydroxide causes decolorization, whereas ammonia produces a brown precipitate.
c) The precipitate is suspended in a calcium chloride solution and chlorine is bubbled through it. A yellow solution of lead tetrachloride is likewise obtained.
WARNING: Yellow solutions containing $PbCl_4$ become dangerously unstable and potentially explosive if heated.

- A solution of mercuric chloride is placed in a Drechsel bottle and treated with a freshly prepared sodium sulfide solution. A black precipitate of mercury sulfide forms immediately. Chlorine is then passed through the mixture. The black precipitate gradually disappears. If the experiment is interrupted for a time, a small quantity of yellow precipitate may be observed in its place. When chlorine is again introduced, this yellow precipitate—identified as a mercury chlorodisulfide of composition $HgCl \cdot 2HgS$—also disappears.

- Water and barium peroxide are placed in a Drechsel bottle standing on a magnetic stirrer. Chlorine is passed through the mixture until the liquid becomes perfectly clear. The solution is then boiled to expel all dissolved chlorine, after which a drop of sulfuric acid is added. An abundant white precipitate of barium sulfate immediately appears. The reaction demonstrates that barium chloride has been formed in solution.

- Ferric hydroxide is prepared by treating ferric chloride solution with ammonia. The precipitate is thoroughly washed to remove all traces of ammonium hydroxide.

It is then placed in a concentrated potassium hydroxide solution through which chlorine is bubbled. Oxygen is evolved and an unstable black or dark wine-colored compound, potassium ferrate, is produced. When dissolved in water, this ferrate yields a red solution. Addition of acid causes oxygen to be evolved and regenerates the original ferric hydroxide.

- A 250 mL flask containing water to approximately one-third of its volume and a few pieces of yellow phosphorus is placed in a hot-water bath. The bath is heated until the phosphorus melts, after which chlorine is bubbled through the liquid. The phosphorus gradually disappears. Upon cooling, if all of the phosphorus has reacted, phosphoric acid is found to have formed. If some phosphorus remains unreacted, the solution contains a mixture of phosphorus-derived acids.

- Chlorine water is poured onto red phosphorus and the mixture is shaken. After allowing the reaction to proceed for about five minutes, the liquid is gently heated to remove excess chlorine. The solution has become acidic owing to the formation of hydrochloric and phosphoric acids. The same result is obtained by bubbling chlorine through water containing red phosphorus.

- When chlorine is bubbled for an extended period through carbon disulfide cooled with ice water, the liquid first turns yellow and then becomes cloudy. Eventually a reddish-brown liquid ring appears, consisting of a sulfur chloride.

- Dry chlorine is passed through carbon disulfide containing a small quantity of iodine. The violet color of the iodine disappears and the liquid becomes a yellow-brown color resembling raw sienna. Its odor is strongly irritating and suffocating. Carbon tetrachloride and sulfur monochloride (S_2Cl_2) are formed. Together they produce sulfur tetrachloride–carbon compounds characterized by an exceptionally unpleasant odor.

- Chlorine is bubbled through carbon disulfide containing a trace of anhydrous ferric chloride. Carbon tetrachloride is formed. Sunlight accelerates the reaction.

- Chlorine is passed through a vigorously agitated mixture of carbon disulfide and water, stirred by a paddle stirrer or a Vibromix-type mixer (Figure 24, page 35) so that the two liquids remain as homogeneous as possible. A lemon-yellow liquid with a suffocating odor is obtained. It consists of a solution of an acid chloride derived from methylsulfuric acid. Crystallization may sometimes be induced by gentle warming in a crystallizing dish.

- Chlorine is passed through formic acid, and the gas leaving the apparatus is bubbled through limewater. The limewater becomes cloudy, while hydrochloric acid can be demonstrated in the first flask.

- Chlorine is bubbled through an aqueous tannin solution. The liquid turns brown.

- Chlorine is passed through a concentrated urea solution, and the gases leaving the reaction vessel are directed into baryta water. The latter soon becomes cloudy because the urea decomposes into carbon dioxide and nitrogen.
Some authors recommend carrying out this experiment with the urea solution at its boiling point. This does not appear to be necessary.

- A Drechsel bottle is charged with perchloroethylene covered by a thin layer of water. A large quantity of chlorine is passed through the apparatus while it is exposed to sunlight. The temperature rises noticeably, and vapors together with crystals appear above the liquid. The mixture is then cooled strongly and its pH tested. The solution is found to be distinctly acidic because trichloroacetic acid has formed.

- Chlorine is passed through concentrated acetic acid containing a small amount of iodine. The liquid, initially violet, becomes deep yellow and eventually develops a golden-yellow color upon cooling. This acidic liquid generally consists of a mixture of mono-, di-, and trichloroacetic acids. Different authors describe this experiment in very different ways. Some recommend performing it in full sunlight, others substitute sulfur for iodine, while still others specify that the acetic acid should be heated under reflux. In reality, the proportions of the various chloroacetic acids formed depend on the duration of the experiment, the temperature, and the intensity of illumination. Although the final yellow liquid has a strong chlorine odor, it does not bleach pH indicator strips, which already indicate a strongly acidic reaction before even touching the liquid surface. By distillation, collecting only the fraction passing over at about 185 °C, it is possible to obtain highly corrosive monochloroacetic acid.

- A large flask is filled with chlorine by displacement of air and covered with a watch glass. The flask is then placed in direct sunlight. The watch glass is lifted, a few drops of ether are introduced, and the flask is immediately closed again. Within seconds, a flame travels through the flask from top to bottom, while the interior becomes coated with finely divided carbon. Hydrochloric acid is formed at the same time. The combustion produces a pressure wave that lifts the watch glass and generates a characteristic sound.

- Chlorine is bubbled for an extended period through ether maintained at approximately 30 °C in a water bath. The vapors leaving the apparatus are passed directly into a condenser. A yellow liquid is collected. When mixed with water, it separates into a colorless layer and a yellow-orange layer. Tetrachloroether has been formed. This substance evaporates rather readily.
The experiment may also be performed by introducing chlorine into ether covered by a layer of water. Under those conditions, various chlorinated derivatives together with acetic acid are obtained.
WARNING: Both experiments must be carried out under very subdued lighting. As demonstrated above, the reaction between chlorine and ether becomes extremely vigorous in bright light or, even more so, in direct sunlight. Ether vapors are also

highly flammable and potentially explosive. The apparatus must therefore be gas-tight and connected to an appropriate exhaust system.

- Connect a glass bottle of at least one liter to a chlorine generator and fill it by downward displacement with the greenish gas. When the odor of chlorine becomes noticeable, indicating that the bottle is full, cover it with a watch glass and reduce the lighting as much as possible. Then slightly lift the watch glass and, using a pipette, introduce a small amount of benzene into the bottle. Nothing happens. Next, switch on a UV lamp beside the bottle. Starting from the side facing the lamp, a white cloud forms and gradually spreads throughout the entire bottle (Figure 83). A few white vapors may escape where the watch glass does not provide a perfect seal. When the bottle is completely filled with white vapors, take it outdoors. A strong insecticide-like odor is released. A mixture of benzene hexachloride isomers has been formed. It was formerly marketed under the name lindane, although only the γ-isomer actually bears that name.
The product may be collected by rinsing the walls of the flask with a small quantity of water. A pH indicator and a few drops of silver nitrate solution show that hydrochloric acid has also been formed.
The same reaction may be initiated by burning a strip of magnesium in front of the flask while it remains in the shade.
IMPORTANT NOTE: Figure 83 is in black and white because under UV radiation the camera produces only falsely colored and poorly legible images. Note that the first and last photographs show the bottle with the UV lamp switched off. The second photograph shows the bottle at the moment the benzene is introduced (vertical streak from top to bottom).

Figure 83

- Chlorine and benzene can also combine in other ways to produce various compounds such as mono-, di-, tri-, tetra-, penta-, or hexachlorobenzene. The products obtained depend strongly on the experimental conditions, including temperature, pressure, illumination, duration, and the presence of catalysts. For example, monochlorobenzene may be prepared by passing chlorine into cold benzene containing a trace of iodine. Hexachlorobenzene (Julin's chloride) may be obtained by passing chlorine into benzene maintained at approximately 80 °C in the presence of aluminum chloride or ferric chloride until no further hydrogen chloride is evolved.

- A large flask is filled with chlorine by displacement of air and covered with a watch glass. A few drops of ethyl acetate are then introduced and the flask is exposed to the beam of a UV lamp. Direct sunlight may also be used. After a short time, the flask fills with a dense white smoke.

- Chlorine is bubbled through a solution prepared by dissolving naphthalene in carbon tetrachloride. The liquid turns yellow and white fumes are evolved. Tetrachloronaphthalene is formed.

- Paraffin is melted in a water bath and chlorine is passed through the liquid. The gas leaving the apparatus is bubbled through a small quantity of water contained in a U-tube to prevent accidental backflow into the hot paraffin. The water becomes acidic and gives the characteristic chloride reaction with silver nitrate, demonstrating the formation of hydrogen chloride.

- Chlorine is bubbled through amyl alcohol.The liquid first becomes yellow and then gradually returns to a colorless state. A noticeable rise in temperature occurs. Amyl chloride and hydrochloric acid are formed.

- Chlorine is bubbled through a glycerol solution. Using bromothymol blue, bromocresol green, or gentian violet—which all change to yellow under acidic conditions—it can be shown that the liquid becomes acidic.
These indicators are preferred because ordinary pH papers are often unsuitable: residual dissolved chlorine bleaches them. Among the products formed are hydrochloric acid and glyceric acid.

- Dry chlorine is bubbled for a prolonged period through absolute alcohol maintained in an ice-water bath. The alcohol first acquires a greenish-yellow coloration. After a considerable time, however, it becomes completely colorless once more. At that point the experiment may be stopped. The resulting liquid fumes in air and exhibits a strongly acidic pH. Impure chloral has been formed, together with hydrochloric acid and other by-products. The characteristic odor of chloral, slightly lachrymatory in nature, is readily recognizable.

- If chlorine is bubbled through a solution of pyrogallic acid, an immediate black coloration appears and hydrochloric acid is formed. The experiment may be performed more simply by mixing chlorine water with a solution of the acid.

- A Drechsel bottle is charged with a mixture of aceton and a small quantity of methyl alcohol. Chlorine, previously washed through water in a separate Drechsel bottle, is then passed through the mixture. A slight white mist appears at first, after which the reaction continues without any striking change in color. After a few minutes, the chlorine supply is stopped and a small quantity of the treated liquid is transferred to a test tube or small flask. A moderate potassium hydroxide solution is carefully added and the mixture shaken. A white vapor again appears and the liquid becomes pink. Addition of more potassium hydroxide, accompanied by

further shaking, gradually changes the color to lilac. Upon standing, the solution slowly turns golden yellow. These color changes are caused by the monochloroaceton formed in the Drechsel bottle.
Before beginning the experiment, it is useful to place a few pieces of calcium carbonate (marble chips) in the reaction vessel to neutralize the hydrochloric acid produced.
Some authors recommend maintaining the Drechsel bottle at approximately 60 °C in a water bath, although this precaution has not appeared necessary in my own trials.

- Dry chlorine, previously passed through sulfuric acid, is introduced into a flask containing toluene and a trace of iodine. The flask is kept cold in an ice-water bath. The liquid develops an intense yellow coloration. The apparatus is then disconnected and the yellow liquid cautiously shaken in the open air while the flask is held with a clamp. Sudden degassing may occur, releasing a substantial cloud that must not be inhaled. The liquid then becomes clear once more and develops an insecticide-like odor.
The outcome of this experiment is strongly influenced by temperature and illumination. Moderate temperatures and subdued light generally give the best results.
In most cases, several chlorinated products will be present simultaneously.
To obtain benzyl chloride as the principal product, the reaction should be carried out in sunlight with the reaction flask maintained at approximately 120 °C and fitted with a reflux condenser. The product must then be distilled, collecting only the fraction boiling between 170 and 185 °C.

- Chlorine may be introduced into a large vessel containing a few drops of turpentine, producing dense black carbonaceous fumes. A simpler method consists of dropping a piece of filter paper soaked in turpentine into a vessel previously filled with chlorine.

- Through the first neck of a three-neck flask, chlorine is bubbled into boiling acetic anhydride. A thermometer is placed in the second neck. The acetyl chloride vapors leaving through the third neck are efficiently condensed, while excess gases are safely vented. The liquid in the flask first becomes greenish and then gradually returns to a colorless state, the acetyl chloride carrying dissolved chlorine with it. Because chlorine is much more soluble in acetyl chloride than in water, the distillate acquires a pronounced green color. The liquid releases vapors that are particularly irritating to the eyes and respiratory tract.
WARNING: It is often forgotten that mixtures of acetic anhydride and water can react violently. The same is true of acetyl chloride and water, the latter producing an immediate and abundant evolution of hydrogen chloride. Consequently, these substances must never be poured into a sink or mixed directly with water.

9.3.1 Bleaching Chlorides and Hypochlorous Acid

Bleaching Chlorides

It was Claude-Louis Berthollet who first studied the bleaching properties of potassium hypochlorite. Berthollet's liquor, consisting of a mixture of potassium hypochlorite and potassium chloride, soon became known as *Eau de Javel* because it was first manufactured on an industrial scale in the village of Javel, near Paris.

Later, around 1820, the pharmacist Antoine Germain Labarraque investigated the disinfecting properties of sodium hypochlorite, giving rise to what was then known as *Labarraque's solution*. These names remained in common use until at least the beginning of the twentieth century.

Subsequently, the manufacturing process for bleach was modified by replacing potassium hypochlorite with sodium hypochlorite. As a result, chemistry books written in different periods often describe completely different compositions for what they nevertheless call *Eau de Javel*. This historical point unfortunately seems to receive little attention from the authors of many textbooks.

Experiments intended to prepare bleaching chlorides are never entirely demonstrative, since the results depend greatly on reaction time, solution concentration, density, and other variables. In practice, mixtures of bleaching agents are often obtained. Nevertheless, the following experiments can be performed without great difficulty.

- Chlorine is passed through:
a) a concentrated solution of potassium hydroxide or sodium hydroxide maintained at 50–60 °C in a water bath. A chloride and a chlorate are formed. Because the chlorate is less soluble, it crystallizes upon cooling.
b) a dilute solution of potassium hydroxide or sodium hydroxide cooled in ice. Under these conditions, hypochlorites are formed.
The bleaching chlorides thus obtained may be demonstrated by briefly heating the solution to expel any dissolved chlorine and then allowing it to act on diluted ink. Silver nitrate may also be used to demonstrate the presence of chlorides.

Additional Experiments

- A large excess of chlorine is introduced through a wide tube into an inactinic flask containing a sodium carbonate solution maintained in ice. The liquid becomes yellow because a mixture containing hypochlorous acid together with sodium chloride, sodium chlorate, and sodium hypochlorite is formed. The experiment is stopped when a sample no longer gives a precipitate with barium chloride, indicating that no alkaline carbonate remains. The resulting liquid possesses strong bleaching properties.

- The preparation of bleaching chlorides is often accompanied by the formation of chlorates, particularly potassium chlorate, which some chemists enjoy preparing for themselves. A convenient method consists of preparing a milk of lime from 30 g of quicklime and 150 mL of water, then adding 10 g of potassium chloride. The mixture is heated to approximately 60 °C in a water bath, and a large excess of chlorine is introduced until a faint pink coloration appears. The chlorine flow is then stopped, and the mixture is heated until the odor of chlorine is no longer perceptible. The liquid is filtered and evaporated in an evaporating dish until a crust begins to appear on the surface. It is then allowed to cool slowly. Potassium chlorate crystallizes from the solution. The crystals are collected on filter paper or cloth placed in a funnel and washed with a small quantity of distilled water. Further purification may be achieved by redissolving the crystals in hot water and repeating the crystallization and washing process.

- Chlorine is bubbled through milk of lime maintained in an ice bath. The lime gradually disappears. If the experiment is stopped before all of the lime has reacted, calcium hypochlorite, $Ca(ClO)2$, is theoretically obtained. In practice, however, it is always contaminated with calcium chloride. If the passage of chlorine is continued, calcium chlorate is formed instead, especially if care is taken to prevent the temperature from rising.
Addition of potassium chloride solution to this liquid produces a double decomposition reaction, causing potassium chlorate to precipitate.

- Chlorine is passed to saturation through a potassium carbonate solution maintained at a very low temperature and protected from light. Sparingly soluble potassium chlorate precipitates immediately. The mixture is allowed to settle briefly, after which the bleaching liquor is decanted and boiled until its volume has been greatly reduced. The hypochlorite it contains is thereby converted into additional chlorate. After a second settling period, the supernatant liquid is discarded and the two portions of chlorate are combined. The solid is washed by adding water and allowing it to settle once more. Fresh water is then added and the mixture is brought to a boil. Upon cooling, purified potassium chlorate crystallizes. The crystals are collected by decantation, the remaining liquid is discarded, and the product is allowed to dry.

- At room temperature, chlorine is bubbled through milk of lime containing a large excess of lime. The reaction is stopped after only part of the lime has been converted, and the flask is shaken vigorously to remove all residual chlorine. A small quantity of cobalt chloride solution is then added, and the flask is fitted with a delivery tube having an internal diameter of about 1 cm and bent horizontally outside the stopper. Upon gentle warming, a steady evolution of bubbles begins. If the glowing tip of a wooden splint is introduced into the outlet tube, it reignites, demonstrating the evolution of oxygen.

- This experiment closely resembles the following one... Cobalt chloride solution is added to a sodium hydroxide solution, producing a pinkish-blue precipitate. The

mixture is heated to approximately 30 °C and chlorine is bubbled through it. The cobalt compound becomes black and oxygen is evolved. This is the same experiment already described on page 88(12) as a laboratory curiosity for the preparation of oxygen.

- The following experiments, performed with household bleach, is particularly instructive. A small flask is charged with bleach and heated until all the liquid has evaporated. A white residue is gradually deposited. When only a small quantity of liquid remains, the heat is greatly reduced and finally removed altogether, allowing evaporation to proceed to completion before cooling. Once the flask has cooled, concentrated sulfuric acid is added dropwise with a pipette. The vigorous reaction that occurs, together with the intense greenish coloration that develops in the flask, demonstrates the presence of at least one alkaline chlorate. The chlorate gives rise to chlorine dioxide, a dangerous gas.
WARNING: Concentrated sulfuric acid must be added slowly to avoid any rise in temperature that could cause the gas to explode. The white residue also contains sodium chloride, which reacts with silver nitrate solution, whereas the chlorate itself does not.

- Pour about 30 mL of concentrated bleach into a 100 mL Erlenmeyer flask. Add 3 to 5 mL of aceton and shake. Considerable heating may occur. Therefore keep some means of cooling the flask close at hand. The contents become milky and then gradually clear while a transparent liquid settles to the bottom. This is impure chloroform containing dissolved chlorine-containing by-products.

Hypochlorous Acid

Hypochlorous acid (HClO), which exists only in solution, may also be regarded as belonging to the family of bleaching chlorides. It is a weak acid but a very powerful oxidizing agent. Addition of hydrochloric acid liberates chlorine. It converts black lead sulfide into sulfate, transforms hydrogen sulfide solutions into sulfuric acid, produces a white precipitate in lead acetate solutions, and gives a black precipitate with manganese salts. It decolorizes most organic dyes, including litmus. At room temperature it reacts with iron powder or steel wool to form a red mixture of chloride and oxychloride while releasing chlorine and hydrogen. With mercury, it produces, after several hours, a deposit of white oxychloride flakes. When heated in contact with it, a polished copper strip loses its shine and becomes yellowish. At room temperature, after several hours, it yields a blue solution and white flakes, while some chemists report the evolution of small quantities of chlorine and oxygen. Magnesium ribbon reacts vigorously, producing large numbers of minute hydrogen bubbles. Zinc and aluminum also react, although much less vigorously. During these various reactions, hypochlorites are generally formed. With manganese sulfate solution, hypochlorous acid produces a black precipitate of manganese dioxide.
When poured onto green chromium oxide, it yields, after several hours, a yellow solution colored by chromic acid. When added to black copper oxide, a pale blue ring

appears around the walls of the test tube after approximately forty-eight hours. If powdered sulfur is immersed in hypochlorous acid and the mixture brought to a boil, the sulfur gathers into a yellow mass while sulfuric acid is formed. The resulting sulfate ion may be demonstrated with barium chloride. A somewhat similar reaction occurs with bleach.

Hypochlorous acid solutions are not stable over long periods, particularly when exposed to sunlight. For preparation and short-term storage, it is best to use inactinic glassware or to work under subdued lighting.

Preparation of Hypochlorous Acid

- Chlorine is bubbled through a solution containing 50 g of sodium bicarbonate dissolved in 600 mL of water maintained at a low temperature. This is by far the simplest and most effective method for preparing a relatively concentrated solution of hypochlorous acid. The use of inactinic glassware is recommended whenever possible.

- Chlorine is passed for an extended period through a Drechsel bottle containing water and powdered calcium carbonate. The vessel is maintained in an ice bath and stirred periodically with a magnetic stirrer. After some time, a yellowish crust appears at the surface of the liquid. The Drechsel bottle is then disconnected and the liquid allowed to stand. It subsequently develops a faint pink coloration. When added to bromothymol blue or bromocresol green solutions, it turns both indicators yellow, demonstrating the acidification caused by the formation of hypochlorous acid.

- Chlorine is bubbled through a sodium hypochlorite solution. Here again, calcium chloride is formed and remains dissolved. If carbon dioxide is used instead of chlorine, however, hypochlorous acid is produced while calcium carbonate precipitates.

- Here is a very simple experiment whose demonstrative value is remarkable. Take two large test tubes and a 150 mL Erlenmeyer flask. Place a large drop of mercury in each test tube. Put a magnetic stirring bar and some boric acid into the Erlenmeyer flask, then place it on a magnetic stirrer. As we have seen, hypochlorous acid may be obtained by treating alkaline hypochlorite with a very weak acid such as carbon dioxide, which forms weak carbonic acid on contact with water. However, boric acid may also be used. Pour bleach into the Erlenmeyer flask and stir. It will be observed that part of the boric acid, which is normally only sparingly soluble, disappears. Stop stirring and pour the liquid into one of the two test tubes, then shake it. Immediately, instead of mercury, a black or brown powder is obtained. Next, pour bleach into the second test tube and shake it. In this case, the mercury merely becomes covered with a thin white layer of chloride. This clearly demonstrates that, in the presence of boric acid, the bleach has been converted into

hypochlorous acid.

- One author explained that hypochlorous acid could be prepared by saturating a neutral sodium sulfate solution with chlorine and then distilling it. According to this author, the first portion of the distillate contains the acid. I carried out this experiment. At first, I obtained a green liquid somewhat resembling chlorine water. I then redistilled it through a Vigreux column and collected everything that distilled over at 95 °C. I did indeed obtain hypochlorous acid in this way, but the method appeared to be of little practical value compared with others already described. It should therefore remain nothing more than a laboratory curiosity. I should also mention that when this solution was poured into bromine water containing KBr, I obtained a brown precipitate with a metallic appearance. It proved to be potassium tribromide (KBr_3), a compound that is seldom mentioned in the literature and is only sparingly soluble in water as well as only slightly affected by cold H_2SO_4.

- In the past, a considerably more concentrated solution of this weak but highly oxidizing acid was prepared from mercury(II) oxide. The oxide was obtained by adding sodium hydroxide to a mercuric chloride solution. The resulting yellow precipitate of mercury(II) oxide behaves in water as the base $Hg(OH)_2$. After prolonged washing with water, the moist oxide was placed in a very large flask—at least two liters in capacity—which was then filled with chlorine by displacing the less dense air. The flask was stoppered and allowed to stand. This operation was repeated many times until a reddish slurry was obtained in which very little oxide remained. Filtration then yielded the desired solution. Most chemistry texts describe this procedure so briefly that the reader gains no appreciation of its extremely long duration, nor of the danger involved in repeatedly inhaling traces of chlorine while refilling the flask by displacement of air. In truth, this method should be avoided. A much simpler alternative is available, although it does not produce so concentrated a solution.
Mercury(II) oxide is suspended in a small quantity of water in a Drechsel bottle, and chlorine is bubbled through the suspension until the oxide has almost completely disappeared. It is important not to wait until every trace of oxide has vanished, otherwise mercury(II) chloride may form and dissolve in the solution as an impurity. The liquid should normally exhibit a pale golden-yellow color and produce a brown precipitate of mercury oxychloride when shaken with metallic mercury. If chlorine water were present instead, a white precipitate would be obtained.

- Dichlorine monoxide, Cl_2O, which is gaseous at ordinary temperatures, may be prepared in a somewhat similar manner. Chlorine is passed through a cooled tube containing pumice stone mixed with mercury oxide that has previously been heated to 300 °C. The product is collected in liquid form at a temperature well below –20 °C because it is highly unstable and explosive.

IMPORTANT NOTE : Many of the experiments described here concerning bleaching chlorides are little more than laboratory curiosities and possess limited practical value.

The last experiment nevertheless deserved mention, although it is far too hazardous to be attempted by anyone lacking extensive practical experience in chemical manipulations.

9.4 Hydrochloric Acid

- Gaseous hydrogen chloride is introduced into a small flask containing 50 to 100 mL of water by means of a tube ending in a flattened delivery tip and fitted higher up with a safety reservoir capable of collecting any water that might otherwise be drawn back toward the gas generator. To minimize the risk of water entering the apparatus, only the final 5 mm of the delivery tube should be immersed. The bulb of a thermometer capable of reading up to 100 °C is placed in the water near the outlet of the tube. As soon as the gas enters the liquid, a characteristic hissing sound is heard. The temperature rises steadily and may easily reach 70 °C.

- A U-tube is filled with water to a level just sufficient to seal the bend and prevent the passage of air. A mark is made showing the initial liquid level in both arms. Hydrogen chloride is then passed through the apparatus for an extended period. The liquid level is found to rise, and the water becomes noticeably warmer. Hydrogen chloride therefore dissolves in water with both an evolution of heat and an increase in volume. The increase in volume may appear unsurprising, but the dissolution of alcohol in water, discussed later, demonstrates that the opposite effect can also occur.

- Hydrogen chloride is passed to saturation through a U-tube containing a saturated sodium chloride solution. Excess gas is vented safely outdoors. Crystals of sodium chloride soon begin to form and settle to the bottom of the tube. The remaining liquid is found to have become acidic.

- Air is passed through a flask containing concentrated hydrochloric acid and then into a solution of potassium permanganate acidified with sulfuric acid and maintained at approximately 70 °C in a water bath. The permanganate first turns brown and then black. After the liquid is allowed to stand, the solid material formed settles to the bottom as manganese dioxide, while the supernatant liquid consists of a highly oxidizing and bleaching solution of hypochlorous acid.

- A U-tube is filled with just enough sodium bicarbonate solution to seal the bend and prevent the passage of air. Gaseous hydrogen chloride is then introduced. The liquid foams and effervesces visibly. Once the effervescence has ceased, the solution is transferred to a porcelain evaporating dish and gently heated to remove the water and expel any excess acid. The remaining salt may then be tasted: it is ordinary sodium chloride. This experiment may be compared with the pedagogical example discussed earlier in the book.

- A small quantity of manganese dioxide is placed in a U-tube immersed in a large beaker containing an ice-water mixture. Ether is then added, followed by a stream of thoroughly dried hydrogen chloride. Careful observation reveals small green streaks produced by an unstable tetrachloride that is soluble in ether. After the experiment and subsequent settling, the ether retains a bluish tint for some time.

- Pass thoroughly dried hydrogen chloride (after drying through sulfuric acid) into aniline cooled in an ice-water bath. At first a cloud of fumes appears, then the liquid becomes pasty. White crystals of aniline hydrochloride, readily soluble in water, soon appear.

- Dry hydrogen chloride, previously passed through sulfuric acid, is introduced into a Drechsel bottle containing turpentine and maintained at approximately –20 °C by means of a crushed ice–calcium chloride cooling mixture. A pronounced darkening of the turpentine is observed, together with the appearance of brown oily droplets.

- A stream of hydrogen chloride is passed through a solution of blue cupric chloride dissolved in ethyl acetate. The liquid changes from blue-green to pale yellow and finally to a rich golden-yellow color.
The same result may be obtained with a solution of cupric chloride in ethyl alcohol, but the solution then becomes cloudy and takes on a camel-hair yellow color.

- Gaseous hydrogen chloride is passed through a concentrated aqueous copper sulfate solution. The solution warms noticeably and gradually develops a characteristic emerald-green coloration, indicating the formation of copper(II) chloride. Sulfuric acid is liberated and may be detected both by pH measurement and by the addition of barium chloride solution.

- A mixture of glycerol and butyric acid is prepared. Hydrogen chloride is bubbled through the mixture. White “clouds” of butyrin can be observed forming within the viscous liquid.

ABOUT BUTYRIC ACID

Butyric acid and hydrogen sulfide share a common characteristic: both possess an extremely unpleasant odor that can be detected at very low concentrations. A single drop of butyric acid spilled onto a floor and absorbed into concrete can render a room malodorous for days. It should therefore be handled with great care.

- Passing hydrogen chloride to saturation through a solution of benzoic acid in methyl alcohol produces a liquid with a pleasant fragrance said to resemble that of guava. The product is methyl benzoate, a material used in perfumery, although many perfumers would describe its scent as being closer to amber. When mixed with salt

water, the liquid yields a white precipitate together with a yellowish oily layer.
A very similar experiment may be performed by replacing methyl alcohol with ethyl alcohol. In that case, ethyl benzoate is obtained, a perfume ingredient often described as possessing a cherry-like fragrance.

9.5 SO_2

In some cases, instead of using gaseous SO_2, its aqueous solution, commonly known as sulfurous acid (H_2SO_3), is employed.

- Sulfur dioxide is bubbled through red wine or, better still, through water lightly colored pink with red wine.
The bleaching effect is readily visible. If the experiment is performed on a dried wine stain on cotton immersed in sulfurous acid, a yellow coloration generally remains.

- Sulfur dioxide is bubbled through water containing a small quantity of zinc powder. An orange-yellow liquid is formed. This is hydrosulfurous acid, H_2SO_2, which precipitates both copper(I) and copper(II) salts while imparting characteristic colors to them. The acid cannot be stored because it rapidly decomposes with the deposition of sulfur.

- Place equal volumes of water and approximately 90% ethyl alcohol in a Drechsel bottle. Add zinc powder and pass sulfur dioxide through the liquid while stirring with a magnetic stirrer. The liquid becomes warm and rapidly turns yellow. Zinc dithionite (hydrosulfite) is formed, giving the liquid its yellow color. If this liquid is mixed with a little hydrogen chloride and heated, a white precipitate forms. A red sulfide may also be deposited in the cool part of the Drechsel bottle.

- Fill a large, perfectly dry bottle with sulfur dioxide by downward displacement. Introduce 2 or 3 mL of nitric acid, then stopper the bottle. It immediately fills with reddish vapors which gradually disappear while white crystals form on the walls. When the bottle is no longer red, open it and add a little water, rinsing the walls. The bottle once again fills with red vapors. When these have disappeared, test the liquid with barium chloride solution. A white precipitate forms. Initially, crystals of nitrosyl sulfate were produced. Upon contact with water, they released the red vapors again and formed sulfuric acid. This provides a simplified demonstration of of the sulfuric acid manufacturing process (see page 148).

- Sulfur dioxide is bubbled through nitric acid diluted with an equal volume of water. Reddish-brown fumes appear. After one or two minutes, the gas flow is stopped and the solution allowed to cool. he liquid then gives a white precipitate with barium chloride solution, indicating the formation of sulfuric acid. Some chemists state that the nitric acid must be heated to between 60 and 80 °C to obtain this result. In my experience, this is only true when the acid is highly diluted. When the acid is diluted

only by half, as described here, sulfuric acid forms readily at room temperature.

- Sulfur dioxide is passed through fuming nitric acid. The acid gradually warms and eventually evolves nitrogen dioxide. Depending on temperature and concentrations, a series of complex reactions occurs. The literature mentions, for example, the formation of crystalline nitrosulfuric acid.

- A continuous stream of sulfur dioxide is passed through a cooled solution of hypochlorous acid previously prepared by bubbling chlorine through a sodium bicarbonate solution. Abundant foaming is observed. The liquid is then brought to a boil to expel dissolved gases, after which barium chloride is added. An immediate and abundant white precipitate is obtained because sulfuric acid has been formed. This experiment is, in my opinion, not entirely conclusive and is open to criticism.

- Sulfur dioxide is passed through chromic acid solution. The color changes to greenish-violet owing to the formation of chromium sulfate.

- Sulfur dioxide is passed through ammonia solution. Ammonium sulfite is formed and tends to crystallize at the outlet of delivery tubes or beneath the gas inlet tube. Tubing of excessively small diameter should therefore be avoided to prevent clogging. The solution may be evaporated and the salt collected. Treatment with sulfuric acid then regenerates sulfur dioxide.

- Sulfur dioxide is bubbled through a sodium hydroxide solution. Sodium sulfite is formed, as demonstrated by the fact that addition of sulfuric acid liberates sulfur dioxide without producing a sulfur precipitate. When the sodium hydroxide solution is highly concentrated—for example, 50 g of NaOH in 100 g of water—the liquid thickens rapidly and becomes pasty.

- A solution prepared from 15 g of potassium hydroxide in 300 mL of water is saturated with sulfur dioxide. A solution containing 38 g of potassium nitrite dissolved in 150 mL of water is then added. After a few minutes, crystals of potassium nitrosulfonate appear and begin to deposit.

- A strongly colored potassium permanganate solution is added to a solution of sulfurous acid. The permanganate is decolorized as it enters the sulfurous acid solution (Figure 84). A famous magic trick is based on this principle. A glass of water—which may even be offered for tasting—is poured into an apparently empty glass whose walls have been coated with a thin layer of permanganate powder. The water instantly appears to turn into wine. The magician's skill lies in calculating the exact quantity of permanganate required to produce a liquid that genuinely resembles wine. This false wine is then poured into a third glass containing a hidden quantity of sulfurous acid. As it flows into the glass, the "wine" gradually

Figure 84

becomes "water" again. Neither the final "water" nor the imitation wine should, of course, be offered for drinking.

- Addition of sulfurous acid to a potassium permanganate solution rendered alkaline with a small amount of sodium hydroxide produces a black precipitate together with sulfuric acid, which may be identified by means of barium chloride.

- Sulfur dioxide is passed through a solution of iodine in methyl alcohol. Depending on the concentration of iodine, the liquid gradually becomes yellow to brown. Iodosulfuric acid is formed, a compound of little practical importance. The resulting liquid reacts vigorously at room temperature with iron and zinc, much more slowly with copper, and not at all with aluminum. After twenty-four hours, the flask in which iron has reacted contains free iodine and iron sulfide.

- An aqueous solution containing potassium iodide and potassium hydroxide is placed in a three-neck flask and heated to slightly above 50 °C. Once this temperature has been reached, a steady stream of sulfur dioxide is bubbled through the liquid. Around each bubble, a brown ring of iodine appears and immediately disappears. The liquid first becomes yellow and then gradually fades. If potassium iodate is to be recovered, the experiment should be stopped at this stage and the solution allowed to cool, since the sparingly soluble iodate will crystallize upon cooling. If the passage of sulfur dioxide is continued, the liquid once again becomes yellow, then brown, and finally violet. At this stage, each bubble of sulfur dioxide produces additional iodine that is no longer consumed by further reaction.

- Sulfur dioxide is passed through an Erlenmeyer flask containing 200 mL of water and a quantity of liquid bromine. The bromine remains at the bottom as a large droplet. The flask is placed on a magnetic stirrer to ensure efficient mixing.The water is rapidly decolorized and the bromine gradually disappears. The mixture is then distilled. At first, an acidic liquid containing dissolved sulfur dioxide is collected, followed by essentially pure water. Finally, a solution of hydrobromic acid remains in the flask. If the temperature is raised to approximately 125 °C, this solution distills to yield hydrobromic acid of about 48% concentration

- Sulfur dioxide is passed through a solution containing both copper sulfate and potassium bromide. A white precipitate of copper(I) bromide is formed. This precipitate dissolves in nitric acid and gradually turns blue upon exposure to air.

- Sulfur dioxide is bubbled to saturation through a concentrated sodium carbonate solution maintained at approximately 40 °C. Upon slow cooling, a large quantity of snow-like crystals separate. If, on the contrary, the sodium carbonate solution is kept cold throughout the experiment in an ice-water bath, the appearance of the liquid changes very little, except that its pH becomes neutral whereas it was strongly alkaline at the beginning.

- A saturated potassium chlorate solution is prepared and a few drops of silver

nitrate solution are added. No visible change occurs. Sulfur dioxide is then bubbled through the solution. A white precipitate forms and turns violet upon exposure to sunlight. The chlorate has therefore been reduced to chloride. The silver nitrate may, of course, also be added after sulfur dioxide has been passed through the solution for several minutes.

- Sulfur dioxide is bubbled through a Drechsel bottle standing on a magnetic stirrer and containing milk of lime. The suspension slowly becomes yellow and then clears completely while warming slightly. The resulting solution consists of calcium sulfite and bisulfite dissolved in sulfurous acid. When added to chlorine water, it immediately destroys both the yellow color and the characteristic odor of chlorine. Calcium sulfite is indeed a very effective dechlorinating agent. If the solution is heated and then allowed to cool, calcium sulfite crystallizes because of its low solubility in water. If the crystals are allowed to settle, the liquid decanted, and a few drops of sulfuric acid added to the white crystals, sulfur dioxide is evolved.

- Prepare a calcium sulfide solution by passing hydrogen sulfide through water mixed with lime. Stop as soon as the lime has disappeared. Boil the solution to expel the excess hydrogen sulfide. Allow it to cool, protected from the air, in a completely filled, tightly stoppered bottle. Once cooled, pour part of the solution into a Drechsel bottle and pass sulfur dioxide through it. Calcium hyposulfite is then formed. Pour this liquid into a sodium sulfate solution. A precipitate of calcium sulfate forms, while the liquid now contains sodium hyposulfite, which decolorizes an iodine solution.

-Sulfur dioxide is bubbled through a brownish-yellow solution of potassium pentasulfide. The liquid becomes golden yellow and cloudy, then eventually turns completely milky owing to the formation of colloidal sulfur. If a solution of iodine in alcohol or water is added, the brown iodine color disappears because, in addition to sulfur, potassium thiosulfate has also been formed.

- Sulfur dioxide is bubbled through a solution of an alkaline sulfide. The solution remains colorless, or becomes colorless if it had previously been yellow due to traces of polysulfides. If a few drops of iodine solution are then added, the iodine is decolorized because thiosulfate has been formed.

- An aqueous solution of sulfur dioxide is prepared and added to a test tube containing freshly precipitated iron sulfide obtained from solutions of iron(II) sulfate and either potassium sulfide or sodium sulfide. The iron sulfide dissolves and the liquid becomes milky owing to the formation of colloidal sulfur.

- Sulfurous acid solution is added dropwise to a copper acetate solution. A yellow amorphous precipitate is obtained. This precipitate is allowed to settle and is then left to digest in a large excess of sulfurous acid solution. Over the course of several days, the precipitate is transformed into a red crystalline copper cuprosulfite and then gradually disappears while the solution slowly acquires a blue coloration.

The experiment may also be performed in a different manner. Sulfur dioxide is passed to saturation through a copper acetate solution, which first becomes apple-green and then pale blue. If the solution is subsequently left to stand for several days in a well-stoppered flask, red crystals of copper cuprosulfite are obtained.
NOTE: If the experiment is stopped while the solution is still green and the liquid is then allowed to stand, a yellow deposit of copper sulfite may eventually appear.

- Sulfur dioxide is passed through hot water containing finely powdered manganese dioxide. The MnO_2 particles gradually disappear while the liquid becomes noticeably warmer. Manganese sulfate is formed. If, on the other hand, the liquid is kept cold throughout the experiment, a different salt is produced: manganese dithionate, MnS_2O_6.

- An aqueous suspension of nickel carbonate is placed in a Drechsel bottle and treated with a large excess of sulfur dioxide. Once the liquid has become less cloudy, it is filtered, yielding a transparent green solution. If this solution is heated to expel all dissolved sulfur dioxide, the nickel sulfite that had remained soluble only in sulfurous acid solution precipitates, giving the liquid a milky green appearance.

Figure 85

- A large test tube is charged with a nickel sulfate solution followed by sodium hydroxide solution. A green precipitate forms. After settling and repeated washing, the precipitate is divided into two portions. The first is treated with ammonia, gradually producing a bluish solution. Through the second, sulfur dioxide is passed to saturation. The suspension first becomes a dull grayish-green and then progressively clears until it becomes a beautiful transparent green solution. When mixed with ammonia, this solution develops a striking blue-violet coloration (Figure 85).

- Sulfur dioxide is bubbled through water containing suspended magnesium carbonate. The liquid becomes transparent because soluble magnesium sulfite is formed.

- Ferric hydroxide is prepared from ferric chloride and ammonia, washed thoroughly, and then treated with sulfur dioxide. The color changes to green owing to the formation of a mixture of iron sulfite and iron dithionate.

- Sulfur dioxide is passed through a ferric chloride solution. Sodium hydroxide is then added. The resulting precipitate is green rather than reddish-brown.
This observation should be compared with the discussion given earlier concerning the preparation of ferrous sulfate. The reaction is already noticeable at room temperature but proceeds even more readily when heated.

-Sulfur dioxide is passed through a solution of copper(I) chloride in hydrochloric

acid. A sulfur precipitate forms and a blue solution of copper(II) chloride appears. The mixture should be allowed to settle in order to observe the result more clearly.

- A dilute copper sulfate solution of pale blue color is prepared and brought to a boil. Sulfur dioxide is then introduced until the color changes to emerald green. The solution is immediately poured into a potassium iodide solution that has previously been boiled to remove dissolved air. A white precipitate of copper(I) iodide is formed. This compound is only very slightly soluble in water or carbon disulfide. If copper sulfate had been allowed to react directly with potassium iodide, a greenish-brown precipitate would have been obtained instead.
The same experiment may be carried out using a light-blue solution of copper(II) chloride acidified with 8% glacial acetic acid. The same color change and the same reaction with potassium iodide are observed.
If the original emerald-green solution is allowed to stand for a long time, a white sulfite gradually crystallizes in the form of fine, attractive crystals. Under subdued lighting, these crystals retain their white color. In direct sunlight, however, they become a very dark red, almost black. When dried, they yield green crystals.

- A yellow potassium chromate solution is placed in a Drechsel bottle and acidified with hydrochloric acid. The color changes from yellow to orange as dichromate is formed. Sulfur dioxide is then bubbled through the solution. The color changes rapidly, first becoming brownish, then opaque olive green, and finally a clear blue-green.
The experiment may, of course, be started directly with a potassium dichromate solution.

- Twenty-five grams of potassium dichromate are dissolved in 150 mL of water, and 8 g of concentrated sulfuric acid are added with stirring while keeping the solution as cool as possible. The solution is placed in a U-tube immersed in an ice bath, and sulfur dioxide is passed through at a moderate rate until a brownish-violet coloration appears. A complex reaction takes place, ultimately yielding chrome alum, which should then be allowed to crystallize.

- A solution of mercuric chloride is brought to a boil. After the flame has been removed, sulfur dioxide is bubbled through the hot liquid. A white precipitate of calomel (mercurous chloride, Hg_2Cl_2) forms immediately. This precipitate would not form under cold conditions. If it is washed thoroughly with water and then heated with water and sodium chloride crystals, the color becomes gray owing to the formation of tiny droplets of metallic mercury.

- Yellow mercury(II) oxide is prepared by treating a mercury(II) chloride solution with potassium hydroxide. The precipitate is allowed to settle and is washed thoroughly. It is then suspended in distilled water and stirred magnetically while sulfur dioxide is introduced. At first, no visible change appears to occur. Then, rather suddenly, the opaque yellow suspension clears and becomes completely colorless and transparent. If the passage of sulfur dioxide is continued, the solution gradually

loses its transparency and becomes grayish owing to the formation of microscopic droplets of mercury. Upon standing, two layers of precipitate are deposited: a gray layer at the bottom surmounted by a white one.

- Sulfur dioxide is passed through a nitrate solution. A sulfate is formed and nitrogen dioxide is evolved.

- Sulfur dioxide is bubbled through a solution of sodium or potassium nitrite. The liquid warms and develops a yellow coloration tending toward brown, depending on concentration. If the experiment is stopped shortly thereafter, the solution filtered, and then allowed to cool, a mixture of complex salts crystallizes. If the passage of sulfur dioxide is continued, the solution eventually becomes colorless and may even begin to effervesce.

- Pass sulfur dioxide through one Drechsel bottle and then through a second one. The first contains vanadium pentoxide in aqueous solution, while the second contains the same compound dissolved in dilute sulfuric acid. The first solution gradually loses its color before developing a very faint bluish tint. The second, on the other hand, turns a distinct deep blue.

9.6 CO

- An ammoniacal silver nitrate solution is prepared by slowly adding dilute ammonium hydroxide to a silver nitrate solution until the precipitate has completely redissolved (see the fourth experiment on page 57 concerning ammoniacal silver nitrate). A stream of carbon monoxide is then passed through the solution. Metallic silver is deposited, causing the liquid to darken, while carbon dioxide is evolved.

- Carbon monoxide decolorizes potassium permanganate acidified with sulfuric acid. At room temperature, the color may first become raspberry-red and then, after standing, leave a deposit while the liquid remains yellowish. The deposit subsequently disappears and the entire solution eventually becomes clear. The reaction proceeds much more rapidly when carried out warm.

- Three Drechsel bottles are arranged in series. The first contains limewater, the second a dilute chromic acid solution of yellow-orange color, and the third baryta water, which is more sensitive than limewater for detecting carbon dioxide. A continuous stream of carbon monoxide is passed through the three bottles. The purpose of the first bottle is to remove any traces of carbon dioxide that might already be present. Gradually, the baryta water in the third bottle becomes cloudy. Carbon monoxide has reacted with the chromic acid, producing carbon dioxide.
Although simple in principle, the experiment is not particularly easy to perform because the reaction is relatively slow and not strongly demonstrative.

9.7 CO_2

- Carbon dioxide is bubbled through limewater. A white precipitate of calcium carbonate forms rapidly. If the passage of carbon dioxide is continued through the cloudy liquid, it eventually becomes clear again because the precipitate dissolves in the carbonic acid formed by the interaction of water and carbon dioxide.
These reactions constitute the basis of the formation of caves, stalactites, and stalagmites.
The experiment becomes even more striking when several flasks of limewater are arranged in series and carbon dioxide is passed successively through them. One can then observe much more clearly the cycle by which the limewater in each flask first becomes cloudy and later returns to transparency.
If baryta water is used instead of limewater, the precipitate consists of barium carbonate, which does not dissolve in an excess of carbon dioxide.

ABOUT SPARKLING WATER

Sparkling water prepared with modern carbon dioxide cartridge systems, now widely available in supermarkets, may be regarded as a supersaturated solution of carbonic acid. Alternatively, naturally sparkling mineral water such as Spa water from Belgium, which contains relatively few dissolved mineral salts, may be used.

- Carbon dioxide, previously washed through water, is passed to saturation through 50–100 mL of household bleach. The operation is stopped when the solution appears to begin evolving gas bubbles. Four test tubes are then prepared. A small quantity of copper turnings is placed in the first two and a little iron powder in the remaining two. Three to four centimeters of the carbon dioxide-treated bleach are added to the first and third tubes, while an equal volume of untreated bleach is placed in the second and fourth. If nothing occurs in the second tube, the first gradually develops a pale blue coloration. Likewise, if a kind of rust appears in the fourth tube, the same phenomenon occurs much more rapidly in the third. Carbon dioxide has converted the bleach into hypochlorous acid.

- Anhydrous ammonia is first passed to saturation through absolute alcohol. The solution is then placed in a freezer in a flask fitted with a stopper allowing a thermometer to pass through. When the temperature reaches approximately 0 °C, thoroughly dried carbon dioxide—previously washed through water to remove any traces of hydrogen chloride—is introduced. The flask rapidly fills with crystals of ammonium carbamate (or ammonium acid carbonate), which is very soluble in water but not in alcohol. In contact with hydrochloric acid, the carbamate decomposes immediately. It also decomposes readily into ammonia and carbon dioxide, both easily identified, when exposed to air or traversed by a rapid air

current.
A variation of this experiment consists of passing carbon dioxide for a prolonged period through ammonia solution. Heat is evolved and a “smoke” is produced, which may be condensed by passing it through a sufficiently wide cooling tube.

- Dry ammonia and dry carbon dioxide are bubbled together, as nearly as possible in equal proportions, through absolute alcohol contained in a flask cooled by an ice–salt mixture. After a prolonged period, the mixture is allowed to stand. Fine white needles of ammonium carbamate gradually appear and may eventually solidify much of the liquid. The crystals may be dried on porous stone if desired.
The experiment may also be carried out without cooling the alcohol, although the yield is lower.

- Basic lead acetate is prepared by dissolving lead acetate in water, adding a small amount of litharge, and heating the mixture. The liquid is then filtered. When carbon dioxide is bubbled through the perfectly clear filtrate, a heavy precipitate of lead carbonate, or white lead, forms immediately. White lead was formerly used by painters as a white pigment.
The chemist Louis Jacques Thénard once recommended adding 7% glycerol to make the liquid more syrupy before introducing the carbon dioxide. I do not recommend this procedure, since the white lead may then solidify into a compact mass that is difficult to remove.
The experiment may also be carried out by dissolving an excess of litharge directly in acetic acid.

- Carbon dioxide is bubbled through undiluted sodium silicate solution. Large transparent "soda crystals," consisting of sodium carbonate, rapidly appear.
Some authors recommend using diluted sodium silicate. This is incorrect, because under those conditions the carbonate dissolves as soon as it forms and no large crystals are produced.
The experiment should nevertheless be kept relatively brief because there is a significant risk that the gas inlet tube will become blocked.

- Carbon dioxide is bubbled for a prolonged period through a potassium chromate solution. The solution becomes orange owing to the formation of potassium dichromate.

- Carbon dioxide is bubbled for a prolonged period through a flask containing water and iron powder that has previously been cleaned with hydrochloric acid. The liquid is then filtered and treated with a solution of potassium ferrocyanide. A green coloration appears, indicating that a small quantity of iron carbonate has been formed.

- A sodium carbonate solution is prepared and one or two drops of alcoholic phenolphthalein solution are added. The liquid develops an intense color. Carbon dioxide is then bubbled through the solution for an extended period. The

phenolphthalein gradually becomes colorless.

- A solution is prepared from 12 g of sodium bicarbonate in 200 mL of water. Not all of the bicarbonate dissolves because the solution eventually becomes saturated. This suspension is placed in a 500 mL flask. One milliliter of the same solution is then diluted with 200 mL of water and placed in a second 500 mL flask. A few drops of alcoholic phenolphthalein solution are added to both flasks. The flask containing the concentrated solution remains colorless when the temperature is between approximately 0 and 15 °C. At 20 °C it becomes only faintly pink. The highly diluted solution, however, immediately develops a strong pink coloration.The concentrated solution is then heated, and the gas evolved is conducted into the flask containing the dilute solution. As heating proceeds, the color of the heated flask gradually shifts toward a red-violet shade, reached at about 50 °C, while the flask receiving the carbon dioxide progressively loses its color.

- Dry ammonia and dry carbon dioxide are bubbled together through a saturated sodium chloride solution. Gradually, and especially upon cooling, the liquid becomes cloudy owing to the formation of sodium bicarbonate.

9.8 H_2S

- Hydrogen sulfide is bubbled through a tube containing a few drops of bromine covered by approximately 10 cm of bromine water. The bromine gradually disappears and the water becomes yellow because of the sulfur formed. The liquid is allowed to stand and is then decanted, preferably protected from light. A solution of hydrobromic acid is thereby obtained. Any remaining hydrogen sulfide may be removed simply by heating the solution. The liquid may also be distilled, since a 48% hydrobromic acid solution distills at approximately 125 °C.
This is the classical preparation of hydrobromic acid solution already described earlier.

- Chlorine and hydrogen sulfide are bubbled simultaneously into cold water contained in a three-neck flask. Sulfur is formed, rendering the liquid milky. The solution also becomes acidic because hydrochloric acid is produced.

- Hydrogen sulfide is bubbled through an aqueous solution of sulfur dioxide (sulfurous acid). A colloidal sulfur precipitate is formed.
The experiment may also be performed entirely in the liquid phase by mixing aqueous solutions of the two gases.

- If equal quantities of hydrogen sulfide and sulfur dioxide are bubbled into warm water, pentathionic acid is formed. By subsequently saturating the solution with barium carbonate and adding alcohol, the corresponding barium salt may be crystallized. This experiment is, however, far from demonstrative.

- Hydrogen sulfide is bubbled through milk of lime. The color gradually changes as calcium polysulfides are formed.

- Hydrogen sulfide is bubbled through bleach. A sulfur deposit forms on the walls of the vessel. At the same time, hydrochloric acid is produced and reacts with the hypochlorite, liberating chlorine.

- Hydrogen sulfide is bubbled through a potassium permanganate solution acidified with a few drops of sulfuric acid. A milky suspension forms because of precipitated sulfur. A manganous salt is also produced. Depending on the concentration of the permanganate, the reaction may yield either a relatively clear liquid or a highly turbid one.

- Hydrogen sulfide is passed first through a flask containing concentrated sulfuric acid and then through a second flask containing a moderately concentrated aqueous potassium permanganate solution. The sulfuric acid becomes cloudy, turns milky, and eventually deposits yellow sulfur. In the second flask, the permanganate is decolorized because it reacts with sulfur dioxide.
The conclusion is clear: hydrogen sulfide must never be dried by passing it through sulfuric acid.

- Hydrogen sulfide is bubbled through a solution of tartar emetic, a mixture of potassium and antimony tartrate long used in medicine, in small doses, as an emetic. A red precipitate is obtained.

- Hydrogen sulfide is bubbled through 33% hydrogen peroxide diluted with an equal volume of water. The solution becomes milky owing to the formation of sulfur.

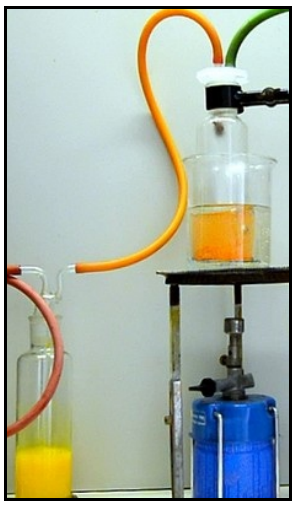


Figure 86

- An aqueous cadmium acetate solution is prepared and divided into two equal portions. The first is placed directly into a Drechsel bottle. A few drops of hydrochloric acid are added to the second portion, which is then placed in another Drechsel bottle maintained at approximately 80 °C in a water bath. Hydrogen sulfide, previously washed through water, is passed first through the cold bottle and then through the heated one. In the first bottle, a blood-red coloration appears initially and gradually changes to canary yellow, coloring the entire liquid. In the second bottle, an orange precipitate forms and rapidly settles to the bottom (Figure 86).

- Hydrogen sulfide is bubbled through a sodium nitrite solution previously acidified with a small quantity of hydrochloric acid. One need not be concerned about the reddish fumes evolved when the acid is first added, although they should not be inhaled. A sulfur deposit appears and fresh reddish fumes are evolved.

- Hydrogen sulfide is bubbled through ferric chloride solution. Sulfur is deposited and ferrous chloride together with hydrochloric acid are formed.

- A Drechsel bottle is charged with a small quantity of water and barium peroxide. A stream of hydrogen sulfide is then introduced. The liquid, initially white, rapidly becomes yellow owing to the formation of soluble barium sulfide.

- A Drechsel bottle is charged with water and strontium carbonate. Hydrogen sulfide is then passed through the mixture. The suspension, initially white, becomes gray owing to the formation of a sulfide. Upon subsequent exposure to air, the material turns yellow.
It is often recommended that the Drechsel bottle be maintained below 10 °C, although I have observed that the reaction also proceeds at ordinary room temperature.

- Hydrogen sulfide is bubbled through a hydrochloric acid solution of mercury(II) chloride. A precipitate first appears, yellowish-white in color, then becomes reddish-brown, and finally black.

- Hydrogen sulfide is bubbled through an aqueous solution of chromic acid. The liquid becomes greenish because green chromium oxide is formed, while sulfur is simultaneously deposited.

- Hydrogen sulfide is bubbled through an acidified potassium dichromate solution. A complex dark mixture is produced, containing polysulfides, sulfites, and thiosulfates, together with a heavy sulfur deposit. The sulfur deposition is even more pronounced when the dichromate solution has not been acidified.

- A solution of arsenious oxide is prepared, a small quantity of hydrochloric acid is added, and hydrogen sulfide is bubbled through the mixture. A yellow precipitate of arsenic trisulfide appears. This compound was formerly known as orpiment.
The sulfide may be collected by allowing the liquid to evaporate in air or in a desiccator. It dissolves readily in alkaline sulfide solutions and also in ammonia.
If sodium hydroxide is added after the sulfide has formed, the precipitate dissolves completely and the liquid becomes clear once more. Subsequent neutralization with hydrochloric acid causes the yellow precipitate to reappear in full intensity.
If, however, the arsenious oxide is dissolved initially in an excess of hydrochloric acid, sulfur is obtained instead when hydrogen sulfide is introduced.
The experiment may also be carried out using aqueous hydrogen sulfide solution.

- A small quantity of arsenious oxide is dissolved in 50 mL of distilled water brought to a boil, producing a solution of arsenious acid. Addition of the aqueous hydrogen sulfide solution causes the liquid to become yellow owing to the formation of arsenic trisulfide. Depending on the concentrations employed, the liquid may remain clear and yellow or become cloudy through the formation of a colloidal precipitate.

- Hydrogen sulfide is bubbled through a lead acetate solution. An immediate black precipitate of lead sulfide is formed.
IMPORTANT: Moist lead acetate paper is the reagent most commonly used for the detection of hydrogen sulfide.

- Hydrogen sulfide is passed through a freshly prepared stannous chloride solution slightly acidified with hydrochloric acid. An immediate brownish-black sulfide precipitate is obtained.

- Hydrogen sulfide is bubbled through boiling nitric acid contained in a two-neck flask fitted with a vertical reflux condenser. Reddish fumes appear immediately. After some time, the apparatus is allowed to cool. The acidic liquid remaining in the flask produces a white precipitate with barium chloride, indicating the formation of sulfuric acid.

- Hydrogen sulfide is bubbled for a prolonged period through water containing suspended barium hydroxide. The liquid slowly develops a grayish-blue coloration due to suspended insoluble sulfide. The mixture is allowed to settle. Most of the liquid is decanted and a few drops of hydrochloric acid are added. The suspension immediately effervesces vigorously, becomes transparent, and releases the characteristic rotten-egg odor of hydrogen sulfide.

- Hydrogen sulfide is passed for a very long time through a flask standing on a magnetic stirrer and containing water together with a small quantity of strontium carbonate. After standing, the liquid is found to have acquired a yellowish-green coloration, while the deposit appears gray-green or even slightly bluish. Strontium sulfide has been formed.

- Distilled water containing powdered molybdenum and previously saturated with hydrogen sulfide is placed in a stoppered flask. A yellow liquid forms rather rapidly. Ammonia has no effect on this solution, whereas hydrogen peroxide decolorizes it.

- Hydrogen sulfide is passed through carbon disulfide. Unstable thiocarbonic acid, H_2CS_3, is formed. It rapidly decomposes once more into carbon disulfide and hydrogen sulfide. The acid may nevertheless be demonstrated by suitable color reactions.

- An alcoholic solution of picric acid is prepared. A small quantity of ammonia is added, after which hydrogen sulfide is passed through the solution for a prolonged period. The characteristic odor of hydrogen sulfide is no longer perceived. The liquid slowly changes from deep yellow to orange and then to red while sulfur is deposited. Picramic acid has been formed.

- Disolve picric acid in ethyl alcohol, then neutralize with a little ammonia. Place this yellow solution in a Drechsel bottle and pass through it, for a prolonged period, a stream of hydrogen sulfide previously washed in water. The liquid gradually turns

blood red because ammonium picrate is formed. Within about 24 hours, this compound slowly deposits as beautiful fine crystals.

Ammonium picrate may also be prepared as follows. Dissolve picric acid in hot water, then this time neutralize with a large excess of ammonia. An excess presents no particular problem. Allow the solution to cool. Crystals are deposited. This method is, however, less convenient than the previous one because it requires a much larger quantity of picric acid at the outset.

DANGERS OF PICRIC ACID AND PICRATES

Moreover, this compound is not only relatively expensive but also dangerous to store in the dry state. Always keep a piece of moist filter paper inside the tightly sealed bottle so that the acid never becomes completely dry

9.9 NH_3

- A rise in temperature is observed owing to the dissolution of ammonia in water.

- A Drechsel bottle is filled to approximately one quarter of its volume with water. Boric acid flakes are added and ammonia gas is introduced. The flakes disappear rapidly while ammonium biborate (tetraborate) is formed. This salt may subsequently be recovered simply by evaporating the liquid.
The experiment may be performed more simply, though less spectacularly, by dissolving the boric acid directly in moderately concentrated ammonia solution.

- Dry ammonia is introduced into glacial acetic acid. At first, a dense white mist forms above the liquid, which becomes increasingly warm. The mist then gradually disappears. Ammonia is allowed to continue entering the liquid for some time after saturation has apparently been reached. The resulting syrupy liquid is a concentrated solution of ammonium acetate. It is preferable to store the salt in this form because it is highly deliquescent.
If the liquid is heated or distilled, it decomposes into acetic acid, ammonia, and acetamide, which is of little practical interest.

- Ammonia is bubbled through a relatively dilute hydrochloric acid solution containing a suitable indicator that changes color when complete neutralization has been achieved. The liquid is then heated and the deposited solid is collected. This solid, ammonium chloride, is ground together with a small quantity of lime. Ammonia is evolved and may readily be recognized by its characteristic odor.

- Thoroughly dried ammonia is passed through a dilute solution of chromic acid.

After some time, the color of the liquid suddenly changes from orange to canary yellow, the characteristic color of the chromate ion as distinguished from the dichromate ion.

- Ammonia is passed through bromine covered by a layer of water. A short, wide outlet tube is connected to a cooled receiving flask or wide tube. The bromine gradually loses its color while white crystals deposit wherever the vapors encounter cold surfaces. When the liquid suddenly becomes completely colorless, the experiment is stopped. Both the liquid and the deposited crystals may be collected. They consist of ammonium bromide. Unlike the reaction between chlorine and ammonia, which may produce explosive nitrogen trichloride, this experiment is completely safe because no nitrogen bromide is formed.
The experiment may likewise be performed by allowing gaseous bromine and gaseous ammonia to react directly. A large three-neck flask immersed in ice water may conveniently be used, the third neck serving to vent any material that does not condense on the walls. The reaction between these two gases, carried out in several different ways, has already been mentioned on page 143.

- A stream of thoroughly dried ammonia is passed through an aqueous potassium permanganate solution. After somewhat less than half a minute, the solution begins to change color and becomes brown. The mixture is allowed to stand and a reddish-brown flocculent precipitate settles out. The pH is then tested and found to be strongly alkaline. A complex mixture has formed, containing Mn_2O_3, KNO_3, KNO_2, KOH, N_2, and H_2O.

- Dry ammonia is passed through a copper nitrate solution. A thick pale-blue precipitate of ammoniacal copper nitrate forms rapidly. If hydrochloric acid is then added, a solution of beautiful emerald-green color is obtained.

- Place a concentrated copper nitrate solution in a Drechsel bottle and pass ammonia through it. The color changes from blue to lilac. As the passage of ammonia continues, the solution finally becomes ink blue. Pour it into a pear-shaped flask and carefully add a large quantity of aceton. The lilac-colored ammoniacal copper nitrate precipitates.

- Ammonia is bubbled through an aqueous nickel sulfate solution. A blue ammoniacal nickel sulfate is formed.

- At least 250 mL of concentrated ammonia solution is placed in a flask and heated gently to generate a large quantity of ammonia gas. The gas is dried thoroughly over quicklime and then bubbled as numerous small bubbles through a solution of resorcinol in ether. After several minutes, the ether becomes cloudy and deposits mauve crystals that absorb moisture when exposed to air.

- A solution of tannin (tannic acid) is prepared in absolute alcohol. Dry ammonia is passed through the solution. Large flocs of ammonium tannate are formed.

If tannin dissolved in diluted alcohol is used instead, oily droplets are obtained.

- A stream of thoroughly dried ammonia is passed through a yellow aqueous turmeric solution. The color changes first to orange and then toward brown.
Water may be replaced with alcohol to prepare an alcoholic solution instead. The reaction is then much more sensitive.

9.10 NO – NO_2 – N_2O_3

- Nitric oxide is prepared by the action of nitric acid on copper and is passed through a tube containing a plug moistened with carbon disulfide. The tube terminates in a burner tip. One waits until all red fumes have disappeared from the gas stream, thereby avoiding the explosive mixture that carbon disulfide vapors could form with air. The gas is then ignited at the burner tip. A very luminous blue flame is obtained.

- A large Drechsel bottle is charged with slightly alkaline water colored blue by bromothymol blue. Nitric oxide is then bubbled through the liquid. The color immediately changes to yellow or yellow-orange owing to acid formation.

- Nitric oxide is passed through hydrogen peroxide. After a short time, the formation of nitric acid may be demonstrated.

- Nitric oxide is passed to saturation through a Drechsel bottle containing a yellow potassium chromate solution until the liquid begins to foam. The solution first becomes orange, then brown, then black, and finally violet. After all remaining nitric oxide has been expelled by passing a large quantity of air through the solution, the final color is found to be blue. Addition of hydrochloric acid, potassium ferrocyanide solution, or potassium ferricyanide solution then produces further color changes—olive green, magenta, and others—depending on how long the reaction had been allowed to proceed.

- An apparatus producing nitric oxide from copper and nitric acid is placed in a large vessel cooled with ice water to approximately 0 °C. Once all red-orange fumes have disappeared and only nitric oxide is being evolved, the gas is passed successively through four wash bottles. The first contains strongly diluted nitric acid. The second contains moderately diluted nitric acid. The third contains nitric acid of approximately 68% concentration. The fourth contains a ferrous sulfate solution. The first bottle develops a pale blue color. The second becomes green. The third turns yellow-orange. The fourth becomes dark brown to black (Figure 87). The first three colors remain stable, whereas the fourth fades rather rapidly through oxidation. If the liquid in the fourth bottle is heated, it immediately releases its dissolved gas and returns to a greenish color. Conversely, if the same liquid is cooled strongly in an ice bath and a substantial quantity of absolute alcohol is added, a complex ferrous salt separates as pale green crystals.

Figure 87

- Sulfuric acid is added dropwise to solid sodium nitrite, and the resulting gaseous mixture (essentially N_2O_3) is directed into a potassium iodide or sodium iodide solution. Iodine is immediately liberated and may readily be identified by means of carbon disulfide, chloroform, or starch.

- Nitrogen trioxide is again produced by the action of sulfuric acid on sodium nitrite and is bubbled into 10–20 mL of concentrated sulfuric acid cooled in an ice-water bath. After a considerable time, small white crystals of nitrosyl hydrogen sulfate begin to appear. Sometimes these crystals become visible only at the end of the experiment, when the flask is shaken in the open air after apparently showing no reaction. They soon disappear, however. In contact with moist air they produce faint reddish fumes. The acid may then be poured into at least twenty times its volume of water and stirred with a glass rod. Reddish fumes are again evolved. Careful observation may reveal fleeting blue colorations caused by the formation of highly unstable nitrous acid in cold water.

Figure 88

- Sulfuric acid is added dropwise to solid sodium nitrite, and the resulting nitrogen trioxide is passed into water cooled by an ice-water bath. The liquid gradually develops a blue coloration owing to the formation of unstable nitrous acid (Figure 88). When poured into a potassium permanganate solution, this liquid immediately decolorizes it. When added to a chromic acid solution or to a sulfochromic mixture, it produces color changes ranging from blue-green to violet, depending on concentration. When added to solutions of alkaline bromides or iodides, it liberates bromine or iodine respectively, while releasing nitric

oxide, which is converted into nitrogen dioxide upon contact with air. It also reduces Fe^3 ions to Fe^2 ions. If, however, a few grains of sand are added to the blue liquid, rapid degassing occurs with the evolution of reddish fumes.
Another rapid and effective method for preparing this unstable nitrous acid from a simple mixture of hydrochloric acid and sodium nitrite solution will be described in Section 12.3.

- Sulfuric acid is allowed to react with sodium nitrite, and the reddish fumes produced are passed first through a Drechsel bottle containing a small quantity of distilled water and then through a second bottle containing hydrogen peroxide. The second bottle is maintained in an ice-water or ice-salt bath because it becomes strongly heated. After some time, the operation is stopped and the apparatus dismantled. The bottle containing water remains cool and produces little foam, whereas the one that originally contained hydrogen peroxide becomes very hot and foams vigorously while evolving reddish fumes. A pH indicator shows that the liquids in both bottles are acidic, but that the solution initially containing water is much less acidic than the one that initially contained hydrogen peroxide. A piece of copper is dropped into each bottle. In both cases the copper is attacked and the liquid becomes blue.The reaction is, however, far more vigorous in the bottle that originally contained hydrogen peroxide. Nitric acid has formed in both vessels.

9.11 C_2H_2

- Acetylene is bubbled through an alkaline potassium permanganate solution. If the solution is only weakly colored, it becomes completely decolorized and black grains of manganese dioxide settle to the bottom. If the permanganate solution is more concentrated, it turns brown because of the large quantity of suspended manganese dioxide particles.
If the solution is strongly alkaline from the outset, it first becomes green owing to the formation of oxalic acid and then subsequently turns brown. Addition of a little calcium chloride solution to the decanted liquid produces a precipitate of calcium oxalate.

- Acetylene, previously washed through concentrated sulfuric acid, is passed through a mixture of dilute sulfuric acid and mercuric sulfate maintained at approximately 80 °C. The liquid develops a pink coloration and acquires an apple-like odor owing to the formation of ethanal.

- Thoroughly dried acetylene is bubbled for several minutes through a chromic acid solution. Carbon dioxide is evolved, and pH measurement shows that the liquid has become acidic.

- Ammonia is added slowly to a silver nitrate solution until the precipitate that initially forms has completely redissolved. Acetylene is then bubbled through the

resulting ammoniacal silver nitrate solution. A canary-yellow precipitate is obtained, rapidly changing to a raw-sienna yellow color. This material is silver acetylide, a toxic and unstable compound that must never be heated or stored. It should be destroyed immediately after the experiment.

9.12 C_2H_4

- Thoroughly washed ethylene is passed through an opaque purple solution of neutral potassium permanganate. The solution darkens markedly. The manganese dioxide formed is allowed to settle. The remaining clear liquid is acidic. Depending on the duration of the experiment, oxalic acid or formic acid may be formed. The liquid also contains other substances, including potassium oxalate.

- Thoroughly washed ethylene is passed through a flask containing bromine water. The reaction takes some time to begin, and the color of the bromine water therefore changes only very slowly at first. Then, rather suddenly, the liquid becomes pale yellow and finally completely colorless. At this point, 1,2-dibromoethane, $CH_2Br–CH_2Br$, has been formed. This compound was formerly known as the liquor of the Dutch chemists.

Chapter 10 - Reactions Between a Gas and a Solid

10.1 Reactions with Air, Oxygen and Hydrogen

Air:

- One of Lavoisier's experiments on the composition of air is famous above all others. In its classical form, a piece of phosphorus is ignited in a small dish resting on a cork float placed on the water of a basin. The entire arrangement is covered by a large tubulated glass bell jar. The phosphorus is ignited with a heated metal rod passed through the tubulure. Dense white fumes immediately appear and, once the bell jar is closed, the water rises inside by approximately one-fifth of the original gas volume. The remaining gas, which no longer supports combustion, consists chiefly of nitrogen.

Although simple in principle, this experiment requires an expensive large tubulated bell jar whose usefulness in the laboratory is otherwise rather limited. Fortunately, another method may be employed. A fairly wide glass tube (more than 1 cm in diameter) is bent and immersed in a water trough, which may simply consist of a PVC container (Figure 89). Near the upper end of the horizontal section of the tube, about 3 to 4 cm from the opening, a small piece of yellow phosphorus is placed. The end of the tube outside the water is then closed with a rubber or silicone stopper. Nothing more is required than patience. The phosphorus slowly combines with the oxygen present in the enclosed air, causing the water level inside the tube to rise. Marks made at the beginning and end of the experiment allow the volume of oxygen originally present in the air to be estimated.

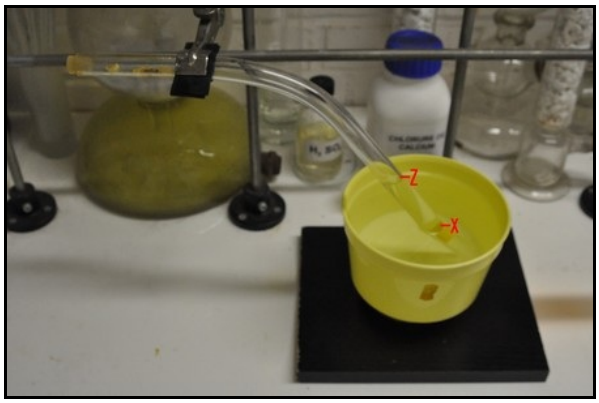


Figure 89

If the room is darkened while the experiment is in progress, the phosphorus may also be seen to glow. This phenomenon gave rise to the term

phosphorescence. It should be noted that the longer the tube, the greater the possible accuracy of the experiment. The apparatus may even be made from transparent plastic tubing.

- A sheet of gold is placed in a solution of sodium cyanide. Nothing happens. If air is bubbled through the liquid, however, the gold disappears within a few minutes through the formation of a soluble gold cyanide complex, commonly referred to as sodium aurocyanide (or sodium auricyanide, depending on the proportions), compounds that have been used in electroplating processes.

- Fit a two-neck flask with a reflux condenser surmounted by a vapor outlet system. Place pieces of copper and concentrated acetic acid in the flask. In the second neck, insert a tube dipping into the acid through which air is introduced by means of an aquarium-type pump. Heat the flask. The liquid first turns sky blue and then duck blue as copper acetate is formed. It may subsequently be recovered as beautiful crystals by evaporation.

Oxygen:

- Using a water trough, several glass bottles of at least 1 liter capacity and having fairly wide necks are completely filled with oxygen and immediately stoppered with rubber stoppers until required. The second stage of the experiment consists of burning, each in a separate bottle, sodium, magnesium, phosphorus, sulfur, and carbon. The substance is placed either in a combustion spoon or in a very small porcelain crucible supported by a wire ending in a horizontal loop. Each substance is first ignited or strongly heated in the open air and then rapidly introduced into one of the oxygen-filled bottles, which is opened at the very last moment. A cardboard disk should be threaded onto the handle of the combustion spoon or onto the supporting wire so that it partially closes the neck of the bottle while combustion is taking place. he first observation is that combustion is far more vigorous and luminous in pure oxygen than in ordinary air. As soon as combustion is complete, the spoon or crucible is removed, about 1 cm of water is poured into the bottle, and the bottle is immediately stoppered again and shaken vigorously. Any fumes present disappear almost at once.
This series of reactions is frequently described in chemistry books to illustrate the distinction between metals and nonmetals. If the resulting solution is acidic, the original substance was a nonmetal. If it is alkaline, the substance was a metal.
Other experiments of the same general type may also be performed. They are, however, much less frequently described, mainly because they are somewhat more difficult to carry out in practice. Iron, for example, requires a different approach. Older books recommended attaching an iron spiral to a piece of burning tinder before introducing it into the oxygen bottle. Since tinder has become difficult to obtain, it is now much simpler to use a small piece of steel wool. Iron powder may also be strongly heated in a tube through which oxygen is passed.
Here are several further examples.

- A bottle of at least 2 liters capacity is filled with oxygen by conventional means. A small quantity of titanium powder is placed in a porcelain crucible held in a loop at the end of a long copper rod and heated to red heat with a blowpipe flame. The crucible is then introduced into the oxygen-filled bottle. The titanium ignites with a dazzling white flame closely resembling that produced by magnesium under similar conditions (Figure 90).

Figure 90

- Using a water trough, a bottle of at least 2 liters capacity is filled with oxygen. Zinc powder is placed in a combustion spoon and covered with a small piece of phosphorus. The phosphorus is ignited with either a blowpipe flame or a red-hot iron rod and, once it has begun to burn, the spoon is rapidly lowered into the oxygen-filled bottle. A brilliant light immediately appears. At first it is yellowish owing to the burning phosphorus, but it soon becomes dazzling white while abundant white fumes are produced. When combustion is complete, the bottle contains dense white fumes that gradually settle on the walls of the vessel (Figure 91). Like the white powder remaining in the combustion spoon, this substance is insoluble in water. It consists of zinc oxide.

Figure 91

Another method may be used with zinc. Zinc powder is placed in a borosilicate glass tube and heated. A stream of pure oxygen is then introduced. A beautiful colored flame appears at the zinc surface, which is rapidly converted into a yellowish-white substance.

- The same type of experiment may be performed with copper powder, which yields a black powder.

- Finely divided vanadium, when moderately heated in a stream of oxygen, ignites also with an intensely bright white flame.Warning: solid vanadium should be heated only in inexpensive glass tubes because it reacts with the glass to form vanadium silicide. The same applies to porcelain crucibles. Any such apparatus should therefore be discarded after use.

- A piece of black selenium about the size of a small pea is placed in a borosilicate glass tube. It is strongly heated while a steady stream of oxygen passes through the tube. The selenium melts and then ignites with a beautiful bluish-white flame. At the same time, fumes of selenium dioxide (SeO_2) are produced and condense along the walls of the tube, which should therefore be chosen fairly long. After cooling, part of the deposit is recovered by rinsing the tube with water. An impure solution of selenious acid is thus obtained. This colorless liquid may then be treated in two different ways. The first consists of adding a solution of sodium sulfide. A red-orange precipitate appears, described by some authors as selenium sulfide and by others as a mixture of sulfur and red selenium. The second method consists of adding sulfurous acid. At first, no visible change seems to occur. However, after shaking the tube, the liquid gradually becomes yellow, then orange, and finally red. A colloidal solution of red selenium is thus formed. On standing, a coating of amorphous red selenium appears on the glass walls.
To clean the tube used for the original combustion, the best method is to pass chlorine through it until all of the selenium has been converted into a white chloride. This chloride then dissolves readily in water, producing a mixture of hydrochloric and selenic acids.

Figure 92

- A flat-bottomed flask of 1 liter capacity (or larger) is prepared by placing a spoonful of manganese dioxide (MnO_2) at the bottom. In two small flasks, prepare separately a solution of sulfur in carbon disulfide and 2 cm^3 of 33% hydrogen peroxide. Place about 1 cm^3 of the sulfur solution in a combustion spoon consisting of a small porcelain crucible supported by a long copper wire and ignite it. As soon as the solution is burning, quickly pour the hydrogen peroxide into the flask and introduce the burning crucible into the neck of the flask.
The oxygen generated by the reaction between MnO_2 and H_2O_2 causes the original blue sulfur flame to become much more vigorous and to change color (Figure 92).
In the preceding experiment, oxygen was generated rather crudely by adding hydrogen peroxide to manganese dioxide. Potassium permanganate crystals may be used instead of MnO_2. However, the reaction is more vigorous, and the flask walls become much more heavily stained with permanganate and manganese dioxide residues. This method is therefore mentioned only for comparison with the preceding one. Figure 93 shows, for example, strontium carbonate.

Figure 93

By using a combustion spoon, various metallic salts may be burned similarly in oxygen after being dissolved, wholly or partially, in ethyl alcohol. The resulting flames display a wide range of colors.
The following examples illustrate this phenomenon:

• Calcium chloride

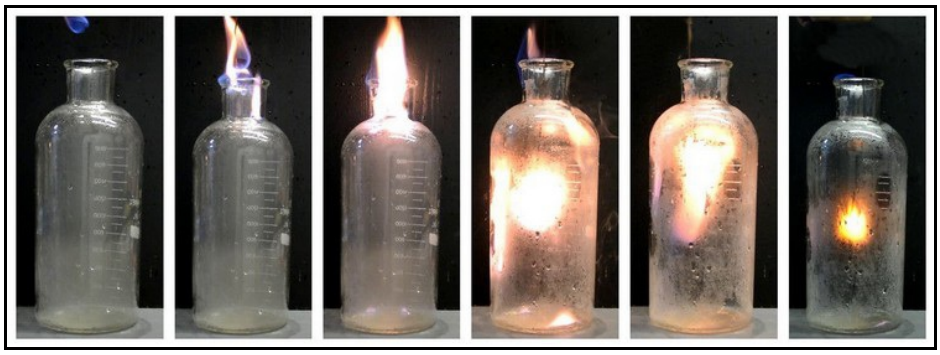
• Barium carbonate

• Copper(II) chloride

• Iron(III) chloride

• Nickel(II) chloride

• Vanadium chloride



Hydrogen

- Place a few pieces of zinc and dilute hydrochloric acid into a small 100 mL flask. Tilt the flask until it is almost horizontal and close it with a silicone stopper fitted with an 8 mm diameter boro 3.3 glass delivery tube partially filled with red iron oxide (Fe_2O_3). Allow the hydrogen to completely fill the flask, then heat the delivery tube. The red powder rapidly turns black. Allow the tube to cool and use a simple magnet to show that this black material is iron. With the very simple apparatus described above, the air is more easily purged from the flask, thereby reducing the risk of an explosion when the tube is heated. A silicone stopper is used because it withstands the temperature reached by the heated tube very well.
The red iron oxide may be replaced with black copper oxide to obtain copper instead.

10.2 Reactions with Halogens

- A strip of magnesium ignited in air burns vigorously in iodine vapor.

- In a long tube made of borosilicate glass 3.3, place two porcelain boats containing, from left to right, iodine and mercury. Close the left-hand end of the tube and attach

an ice pack to the opposite end. Begin by heating the section containing the mercury. As the metal begins to quiver and produce fine droplets that condense farther along the cooled wall of the tube, heat the boat containing the iodine. A violet cloud spreads through part of the tube and passes over the mercury. Yellow and green deposits then begin to appear on the walls of the tube. Upon cooling, red areas of mercury oxide may also be observed. The principal product, however, is mercuric iodide.
At room temperature, a drop of mercury also reacts with the iodine vapor contained in a bottle. This produces green or red spots of mercury iodides.

- Place a few iodine crystals in a narrow-necked Erlenmeyer flask of approximately 500 mL capacity. A small piece of yellow phosphorus is placed in a miniature crucible supported by a wire ending in a loop and lowered to about the middle of the flask. The flask is loosely covered with a piece of cardboard and placed on an electric hot plate so that iodine vapor quickly fills the vessel. When the vapor reaches the phosphorus, the latter ignites.

- Assemble a reflux apparatus (Figure 94) consisting of a flask fitted with a condenser. Place a piece of cobalt and some concentrated bromine water in the flask. Heat the flask while operating the condenser. The upper end of the condenser should be connected to a tube capable of carrying any escaping bromine outdoors or into a fume hood. As the temperature rises, the flask first fills with red vapor. Then, little by little, and without any noticeable decrease in the liquid volume, the red-orange coloration disappears. Once the flask has been completely cleared of this color, disconnect it from the condenser and allow the liquid to continue boiling so that part of it evaporates. The remaining solution has a pink coloration owing to the formation of a small amount of cobalt bromide. A few drops of chlorine water added to this solution immediately produce a strong yellow color as a result of the partial liberation of bromine.

Figure 94

- An Erlenmeyer flask of about 1 liter capacity may be filled with bromine vapor simply by holding it at an angle over a bottle of liquid bromine. Once the flask has acquired a deep orange color, introduce a small piece of phosphorus placed in a tiny porcelain crucible supported by a copper wire ending in a loop.

The phosphorus rapidly ignites.
The same reaction may be carried out using liquid bromine directly, but it then becomes considerably more hazardous and should be performed only under the following conditions. Pour a small quantity of liquid bromine into a long test tube about 25 mm in diameter, mounted at an angle and wrapped with adhesive tape. Using tongs, drop into it a piece of phosphorus about the size of half a small pea.The phosphorus ignites and may even be ejected from the test tube before falling several meters away. Needless to say, nothing and no one should be located along its possible trajectory. The adhesive tape serves as a precaution in the event that the test tube should shatter, helping to prevent fragments from being scattered in all directions.

- Place approximately 1 cm^3 of bromine in a small test tube fitted with a ground-glass stopper. Then add several pieces of sulfur, which disappear one after another. A very dark red liquid sulfur bromide (S_2Br_2) is formed. It has a somewhat oily appearance, fumes slightly in air, and possesses the same unpleasant odor as sulfur chloride.This liquid decomposes slowly in cold water, producing a mixture of acids while releasing hydrogen sulfide. It should never be heated, as its decomposition may be explosive.
Two or three drops of aceton added to two or three drops of this bromide produce a yellow solution of sulfur.

- Pass bromine vapor over iron filings heated in a glass tube. The iron becomes incandescent, and microscopic crystals of iron bromide deposit in the cooler portion of the tube. In the heated region, the glass acquires a reddish-brown coloration and is permanently damaged.

- A strip of magnesium burns in bromine vapor, producing dense white fumes.

- Pour a small quantity of liquid bromine into a fairly tall test tube and then drop in a small ball of aluminum foil. The reaction does not begin immediately, which may create a dangerous illusion because one should avoid approaching the tube for a closer look. Suddenly, however, the highly exothermic reaction starts and flames become visible. Allow the reaction to proceed until the bromine has disappeared and the apparatus has cooled. A small amount of water is then added with a wash bottle. Crackling sounds can be heard.
If, instead of pure bromine, the aluminum ball is introduced into highly concentrated bromine water, the reaction proceeds much more slowly. About ten minutes are required before the liquid becomes cloudy and subsequently develops a dirty greenish-yellow coloration.

- Pass bromine vapor over molten tin contained in a glass tube having a slight bend in which the metal can collect. White fumes are produced. The glass generally remains stained.

- Place a small quantity of antimony powder in a tube made of boro 3.3 glass and

heat it. Bromine vapor is then passed over the antimony by gently warming Br_2 in a small flask connected to the tube. White fumes of antimony bromide are observed. Heating is not, however, essential for antimony to react with bromine. If a small quantity of liquid bromine is poured into a long test tube held vertically and protected as a precaution by a wide band of transparent adhesive tape, a piece of antimony may then be dropped into the bromine with the aid of tongs. A very vigorous reaction initially occurs, accompanied by sparks and sometimes even by an explosion or by projections of material. The reaction then continues more quietly, although still quite audibly. A calmer version of the same experiment may be obtained by first diluting the bromine in carbon disulfide.

- Place a small quantity of arsenic powder in a tube made of boro 3.3 glass and heat it while passing a stream of bromine vapor through the tube. White fumes appear owing to the formation of an arsenic bromide.
Heating is not actually necessary for obtaining arsenic tribromide ($AsBr_3$). If a small quantity of liquid bromine is poured into a long vertically mounted test tube and a piece of arsenic is then introduced, a vigorous reaction immediately takes place, producing the bromide.

- Pour a little more than 1 cm of liquid bromine into a long, narrow test tube and then add titanium powder that has just been heated to red heat. From that moment onward, faint crackling sounds may be heard continuously, while bright sparks appear sporadically at the surface of the bromine. Although spectacular, the reaction proceeds very calmly for many minutes. It is even more impressive in the dark (Figure 95).

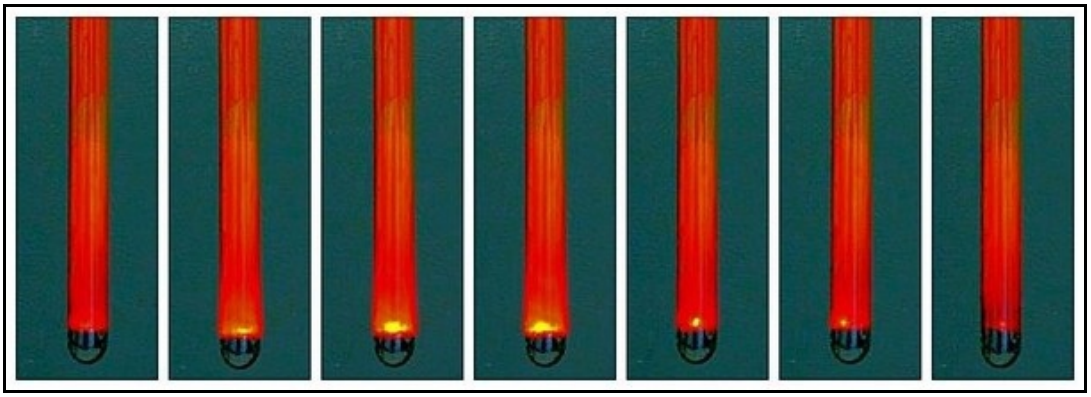


Figure 95

At the end of the experiment, use a wash bottle to direct a jet of water into the test tube and then flood it thoroughly before handling it again.
The same experiment may be carried out in a slightly different manner. A long test tube is clamped vertically and charged with 1 to 2 cm^3 of bromine. A small quantity of cold titanium powder is then added and the bromine is warmed gently. As soon as the first spark is observed, heating is discontinued and the reaction is allowed to proceed on its own. It gradually accelerates. Eventually it reaches a climax: the flames become more intense and a thick yellow fume is evolved. The reaction then

subsides, although small flickering flames continue to dance about in the test tube for quite some time. When the experiment appears to be completely finished, a jet of water should nevertheless be directed into the tube with a wash bottle in order to ensure that it can be handled safely for cleaning (Figure 96).

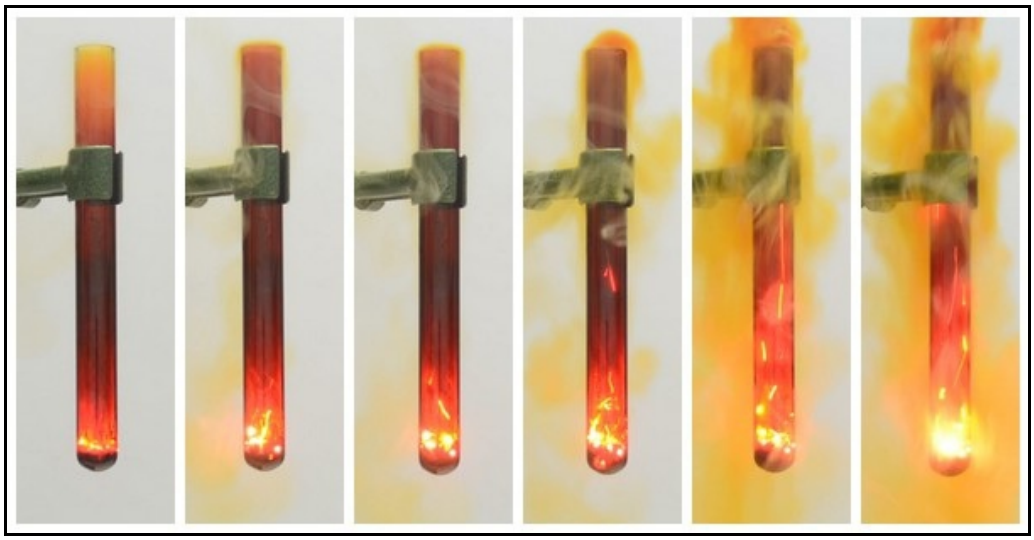


Figure 96

- Pour a small quantity of bromine onto a few drops of mercury in a sturdy, fairly long test tube. The reaction is initially slow but gradually becomes more vigorous. Depending on the quantities and proportions employed, it may become quite energetic and potentially hazardous. In any case, one should remain at a safe distance until only a white powder of mercury bromide remains.
The reaction may proceed more slowly and less vigorously if concentrated bromine water is used instead of liquid bromine. In that case, the mercury gradually becomes swollen and roughened.

- Place a small amount of bromine water in the bottom of a footed test tube and then fill the remainder of the vessel with bromine vapor simply by holding a bottle of bromine above it. Once the test tube has become uniformly red throughout its height, strongly heat a copper wire and plunge it into the vapor. White fumes immediately appear. A white deposit also forms on the copper spiral. If the spiral is reheated afterward, it gives off dense vapors. When the bromine water is poured out of the test tube, a white substance can be seen adhering to the walls. This substance is copper bromide.

Figure 97

The reaction between bromine and copper may also be carried out in the liquid phase at room temperature. In this case, bromine water is placed in a tightly stoppered bottle containing a copper spiral. A green coloration gradually appears around the copper, indicating the formation of copper bromide. With occasional shaking, the entire solution becomes green in less than a day and subsequently turns blue (Figure 97).

- The action of bromine on bismuth is dangerous and should therefore be carried out as follows. Pour a little less than one centimeter of ether into a 100 mL Erlenmeyer flask or flask. Then add 1 or 2 mL of bromine and shake. Finally, drop in a piece of bismuth about the size of half a split pea. The liquid rapidly becomes cloudy and turns orange. After standing for a short time, two layers become visible: a denser blood-red lower layer and an upper layer that is only faintly yellowish. Upon shaking, this second layer even becomes colorless as the bromine disappears completely. The denser layer is a solution of bismuth tribromide in ether. The contents of the flask fume in moist air while giving off a pleasant odor which should nevertheless not be inhaled.

- Place a small quantity of liquid bromine in a Drechsel and a little solid phenol in a second Dreschel of normal size. A steady stream of air is passed through the first one and then into the second, carrying bromine vapor over the phenol. The phenol liquefies, and bromophenol is formed. The product is soluble in alcohol.

- A test tube approximately 25 mm in diameter and 25 cm long is first filled with carbon dioxide by displacement. A piece of yellow phosphorus about the size of half a pea is then introduced. The tube is fitted with a two-hole stopper, one opening allowing the passage of a glass tube ending about 5 cm above the phosphorus. Chlorine is introduced through this tube. White fumes first appear, after which the phosphorus ignites. Depending on the proportions of chlorine and phosphorus employed, the final product is either a liquid or a solid, both of which produce abundant white fumes on contact with water.

- Red phosphorus also ignites in chlorine. The following procedure using a large footed test tube, as tall as possible and having a capacity of at least 1 liter (Figure 98) produces an experiment that may be even more spectacular than the preceding one.

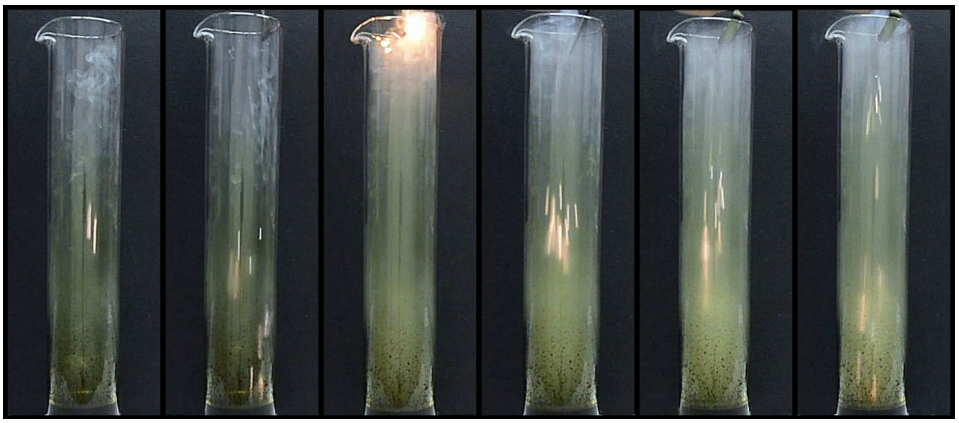


Figure 98

Pour concentrated hydrochloric acid into the bottom to a depth of approximately 15 mm. Then add one or two spoonfuls of potassium permanganate, or alternatively a few pieces of solid swimming-pool chlorinating compound, and wait for the chlorine to rise toward the top of the tube. Its presence is revealed first by its

greenish color and eventually by its odor. Using a small spatula, introduce a little red phosphorus into the center of the tube. The phosphorus should first be crushed to avoid the formation of lumps. As soon as the particles encounter the chlorine, they ignite and form small descending meteors. If the spatula is held too close to the mouth of the tube, the phosphorus remaining on its surface may ignite before it even falls. The test tube gradually fills with a dense white fume.

- Red phosphorus ignites also when exposed to a stream of chlorine flowing through a tube. Phosphorus trichloride is formed and, provided that a sufficient quantity of phosphorus has been used, may be collected as a liquid in a well-cooled receiver. The phosphorus should not be placed in a single heap, however, as this may be dangerous. It is preferable to disperse it among Raschig rings or mix it with pumice stone. Only high-quality ground-glass apparatus should be used, and rubber stoppers must be avoided.

- Bleaching powder was mentioned earlier as a substance formerly used for the production of chlorine. As a matter of curiosity, it may be interesting to observe its formation in the laboratory. The most delicate part of the experiment consists in moistening slaked lime without adding too much water. The best procedure is to place a quantity of slaked lime in a large PVC jar and lightly spray its surface with a small perfume atomizer. The material is then mixed by shaking the jar and sprayed again. The operation is repeated until small agglomerated pellets of lime begin to appear. The prepared lime is then placed in a long glass tube fitted with ground-glass joints at both ends and mounted horizontally in a clamp. One end of the tube is connected to a chlorine generator and the other to a fume hood or another suitable exhaust system. These connections should be made using ground-glass fittings attached to flexible rubber tubing or, preferably, PVC tubing. This arrangement makes it easy to rotate the tube periodically about its axis without disconnecting it from either the chlorine generator or the exhaust line. When chlorine is introduced, a change in color soon becomes apparent inside the tube. The tube also becomes noticeably warm, and a mist begins to appear. These changes first occur near the chlorine inlet and then gradually move toward the outlet while the portions that were previously hot cool down slowly. It may be useful to cool the outside of the tube periodically with a cloth soaked in cold water. In practice, nearly all of the chlorine is absorbed until the reaction zone reaches the outlet end of the tube. When this final portion also begins to cool, the reaction is complete throughout the entire tube and it may be disconnected from the chlorine generator.
A simple test shows that the yellowish material now present in the tube releases large quantities of chlorine when brought into contact with hydrochloric acid. Unfortunately, even when stored in perfectly airtight PVC containers, its shelf life remains rather limited.

- A small quantity of black selenium powder is placed in a bulb tube through which a stream of dry chlorine is passed at room temperature. At first, the selenium may appear to melt and become a reddish-brown liquid. It then warms up and gradually turns white. Long time is required for the entire mass to become white, and the

chlorine generator must therefore be capable of supplying chlorine for an extended period. Once only a white mass remains, the tube is rinsed with distilled water and the liquid allowed to settle. If a solution of sodium sulfide is added, a rather heavy orange precipitate is obtained.
If the white solid is heated, it first turns yellow and then gives off yellowish vapors of selenious acid.
In this experiment, liquid dark-brown selenium monochloride is formed first. In the presence of excess chlorine, it is converted (according to Berzelius and to the *Traité de Chimie Minérale* of Paul Pascal and collaborators) into selenium dichloride and then into white selenium tetrachloride, Se_2Cl_4 , which decomposes in contact with water to produce selenious acid and hydrochloric acid (Figure 99).

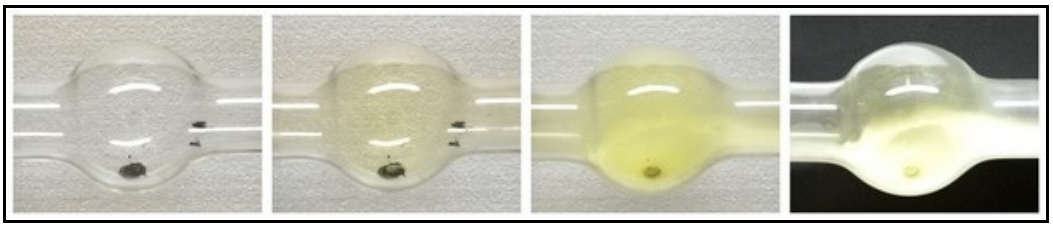


Figure 99

A different way of carrying out the same experiment is as follows. A small quantity of black selenium reduced to powder in a mortar is placed in a Drechsel bottle and lightly moistened. A stream of chlorine is then introduced. The selenium appears to melt into a red liquid (Se_2Cl_2). The Drechsel bottle is opened and several centimeters of water are added. The chlorine stream is then resumed and bubbled through the liquid. The brick-red liquid slowly becomes completely colorless. The experiment is stopped at this point and the Drechsel bottle is aired. The resulting colorless liquid is found to have a very low pH. It consists essentially of a mixture of hydrochloric acid and selenic acid. It may be necessary to warm the liquid slightly to expel traces of dissolved chlorine that could otherwise bleach indicator paper.
NOTE: Selenium, like sulfur and phosphorus, can exist in several different forms. One may therefore encounter black, red, or gray selenium, as well as various colloidal forms. These varieties possess different physical and chemical properties.

- Many chemistry books state that sodium ignites when brought into contact with chlorine at room temperature, producing sodium chloride. In reality, this occurs only when the sodium has been divided into very small fragments. Otherwise, sodium chloride forms only slowly on the surface of the metal.
To observe this, place a piece of sodium about the size of a small pea on a bed of sand at the bottom of a large bottle (2 liters or more) previously filled with carbon dioxide. The bottle is then filled with chlorine, which displaces the carbon dioxide, and is closed with a watch glass. Then, using a long glass rod dipped in water, touch the sodium. The metal immediately ignites with a reddish-yellow flame while reacting with the chlorine. A dense white cloud of sodium chloride is produced (Figure 100).

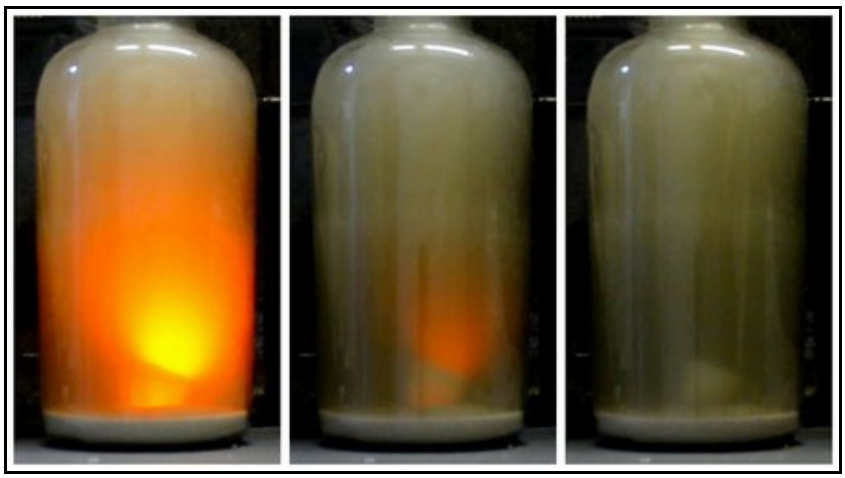


Figure 100

- Some chemistry books state that manganese is so reactive with chlorine that it reacts with it at room temperature. This is not what I observed. On the contrary, I had to heat the manganese in the tube through which chlorine was passing before the small pieces of metal suddenly became incandescent. The reaction then propagated through the sample, leaving behind a dark molten material that soon solidified. Cleaning the tube afterwards required the use of aqua regia.

- Chlorine is passed over molten sulfur contained in a bulb tube fitted with a ground-glass joint and prolonged by an adapter leading to a small receiver cooled with ice water. A reddish liquid having a highly unpleasant odor is collected. This liquid is disulfur dichloride (S_2Cl_2), which is soluble in benzene and chloroform.
Many chemistry books seem to suggest that this experiment can be carried out with a tube and condenser fitted with rubber stoppers. This is incorrect because sulfur chlorides attack rubber severely. If a fully ground-glass apparatus is unavailable, cork stoppers may be used as a last resort. However, they do not guarantee a gas-tight system, and one should remember that sulfur chlorides produce abundant toxic fumes when exposed to air.
According to certain chemistry manuals, the same product may be obtained simply by passing chlorine over solid sulfur at room temperature. Some authors add that the experiment should preferably be performed in direct sunlight, but they provide few practical details concerning either the procedure or the duration of the operation. The following description is therefore intended to fill that gap.
The experiment must be carried out in strong sunlight. Since chlorine attacks rubber and is extremely harmful to the environment, only glass or PVC connections should be used. Provision must also be made for absorbing any unreacted chlorine rather than releasing it directly into the atmosphere. Finally, because the operation generally requires more than twenty minutes, the chlorine generator must be capable of producing substantial quantities of chlorine over an extended period. The chlorine generator should preferably be based on the action of hydrochloric acid on trichloroisocyanuric acid ("solid pool chlorine") and should be followed by a Drechsel wash bottle containing a small quantity of water (not shown, on the right-hand side of Figure 101). The principal part of the apparatus, where the

reaction takes place, consists of a long glass tube or, preferably, a silica tube (t), mounted in an inclined position with the chlorine inlet at the lower end. At this point is attached an adapter resembling a Drechsel head whose dip tube has been cut very short. Through this tube (e), chlorine enters the reaction vessel, while the second tube of the pseudo-Drechsel head, inclined downward (s), allows the liquid disulfur dichloride formed during the reaction to flow into a small receiving flask. At the upper end, the sulfur tube is connected by PVC tubing to a one-liter Drechsel wash bottle containing a sodium hydroxide solution (L). This solution absorbs a large proportion of the chlorine and thus prevents it from being discharged into the atmosphere. A considerable time is required before the sulfur begins to change color. It then becomes glossy and gradually releases a tangerine-colored liquid. When this liquid starts to accumulate at the lower end of the sulfur tube, it may be useful to increase the inclination of the apparatus progressively in order to facilitate its flow into the receiving flask. The experiment should be stopped while some sulfur still remains in the tube. Otherwise, a secondary reaction may occur. In the presence of excess chlorine, a redder product may form, consisting of a dimeric mixture of S_2Cl_2 and SCl_2.

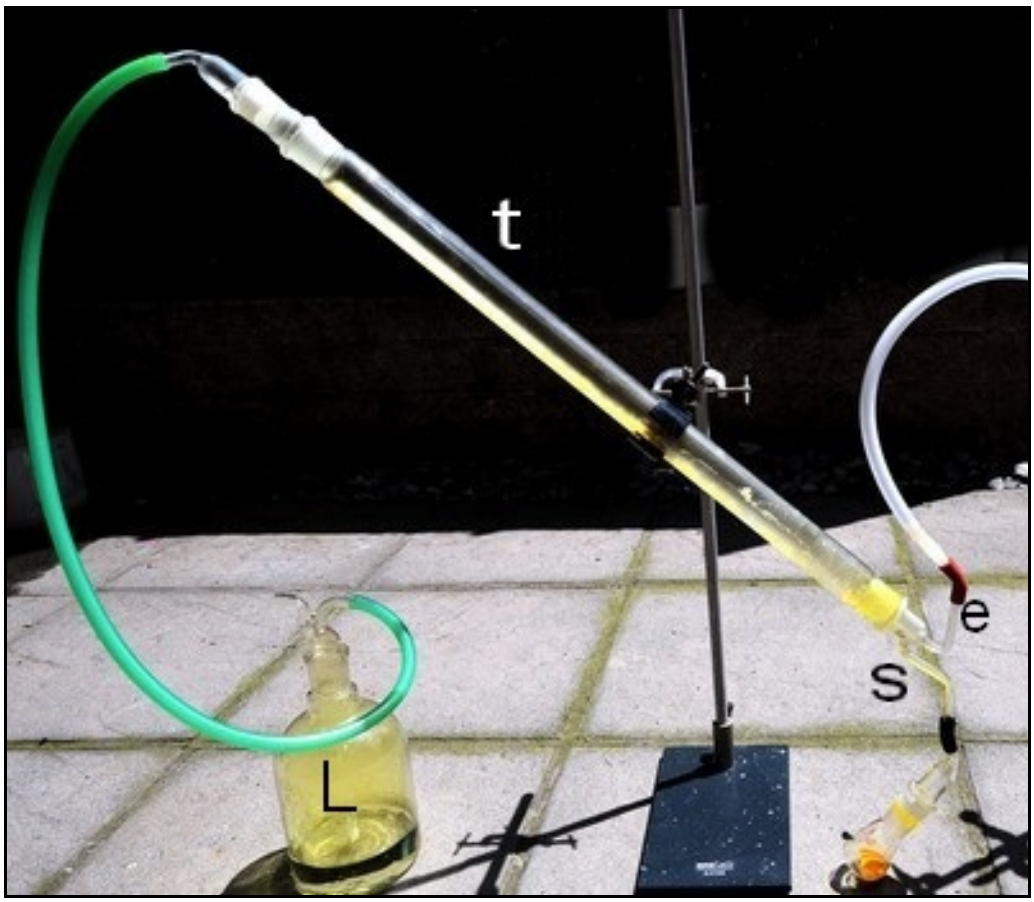


Figure 101

As soon as the receiving flask is disconnected, it should be closed immediately with a ground-glass stopper fitted with a PTFE seal. The contaminated glassware may then be cleaned with aceton.

Disulfur dichloride decomposes in contact with water, dissolves phosphorus, and may react violently with certain metals.

- Chlorine is passed through boiling water and then through a refractory tube heated to red heat. Hydrogen chloride is produced and may be identified by any of the methods described previously.
WARNING: In practice, chlorine must be generated using the special stopcock funnel shown in Figure 57 page 111. If an ordinary dropping funnel were used, the pressure inside the flask containing the boiling water would force the chlorine to escape through the chlorine generator rather than pass into the boiling flask. To prevent water vapor from condensing inside the refractory tube, the tube should be given a slight inclination so that any condensed water flows back toward a hot zone where it can be revaporized. Unfortunately, such practical precautions and arrangements are rarely mentioned in chemistry textbooks, which are often more concerned with theory than with laboratory practice.

- A very thin layer of iron powder is placed in a tube made of boro 3.3 glass or silica. The powder is warmed slightly while a stream of chlorine is passed over it. Brown fumes appear and condense as a brown coating on the cooler walls of the tube or in a receiver placed beyond it. The iron powder itself become yellowish-brown. Both the powder and part of the brown deposit are dissolved in water and tested separately with sodium hydroxide solution, ammonia solution, and finally potassium ferrocyanide solution. The resulting precipitates are identical in color to those obtained from ferric chloride.
The same experiment, with identical results, may be carried out using Fe_3O_4 instead of metallic iron.
The same reaction may be demonstrated in a simpler manner. A large footed test tube is charged with enough household bleach to form a layer 2 to 3 cm deep at the bottom. Hydrochloric acid is then added, causing the test tube to fill with chlorine. Once the vessel is filled with the gas, an iron spiral heated to red heat in the flame of a Bunsen burner is introduced. Brown droplets immediately detach themselves from the iron and fall into the liquid, while red fumes spread throughout the test tube.

- Many chemistry books state that moist chlorine reacts at room temperature with copper wire or copper powder and may even ignite the metal. This is far from true, if not entirely false. In reality, hot water vapor and chlorine are required. In practice, a chlorine generator is followed by a flask containing water heated almost to boiling. The chlorine is bubbled through this water and then passed into a bulb tube containing either copper powder or well-cleaned copper wire. As water droplets condense inside the tube, they gradually acquire a green coloration due to the presence of copper chloride. The bulb tube should be inclined slightly toward the chlorine inlet so that condensation occurs preferentially in that region rather than farther along the tube.

- A combustion tube made of boro 3.3 glass is used. It resembles a large footed test

tube approximately 50 cm high and 6 cm in diameter. A small side arm is located about 5 cm above the level of the flat base. A small quantity of chlorine water is placed in the bottom of the tube and a stream of chlorine is introduced through the side arm. Once the combustion tube is filled with chlorine, a copper wire previously heated to red heat is lowered into it. Brown fumes immediately appear and the wire seems to melt into glowing droplets that fall into the chlorine water while the incandescence gradually spreads upward along the metal. When the tube has become filled with brown fumes, the copper wire is withdrawn and the vessel is stoppered before being shaken. The fumes then dissolve in the chlorine water. The resulting liquid is poured into a beaker, warmed gently, and stirred until the odor of chlorine disappears. The remaining solution is a beautiful transparent emerald green. However, when diluted with water, it becomes blue, like a solution of copper sulfate. It is in fact a solution of cupric chloride.
If brass wire is used instead of copper wire, the fumes are more yellow and numerous red sparks are emitted in all directions (Figure 102).
If a tube such as the one shown in the illustration is unavailable, a Woulff bottle fitted with a lower side arm or even a graduated cylinder may be used. In the latter case, chlorine may be introduced through a tube inserted into the cylinder or generated directly within it by adding hydrochloric acid to bleach placed at the bottom instead of chlorine water. Although the resulting saline solutions will not be pure, their colors remain clearly visible.

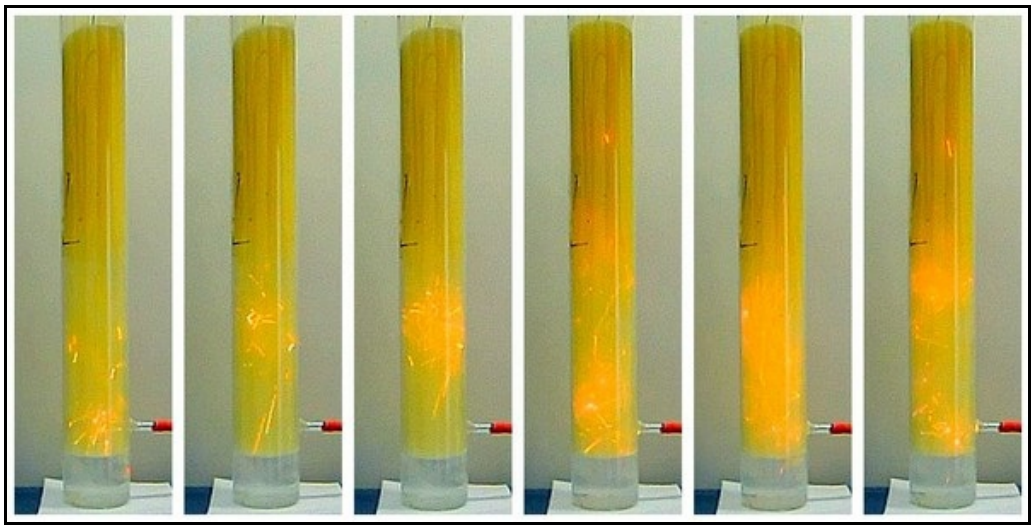


Figure 102

- Place some zinc powder in a tube made of boro 3.3 glass and pass a stream of chlorine through it. Warm the zinc gently. It then reacts vigorously, producing dense white fumes of zinc chloride.
The same experiment, with the same result, may be performed using zinc oxide instead of metallic zinc.

- Place granulated tin in a three-neck flask and heat it until it melts. Chlorine gas is then introduced through a tube dipping into the molten tin or terminating just above

its surface. White vapors are produced and pass through a conventional condenser before entering a receiver cooled with ice. The arrangement therefore resembles, to some extent, a distillation apparatus, and ground-glass joints rather than stoppers are essential. A yellow liquid is collected. This is tin chloride, also known as Libavius' fuming liquor, a substance whose preparation by a slightly different method was described earlier on pages 121 and 122. If water is poured into this liquid, a crackling sound is heard, abundant fumes are evolved, and the reaction gradually subsides.

- Place a small quantity of magnesium powder in a tube and pass through it a steady stream of chlorine that has previously been bubbled through water maintained at approximately 60–70°C. The magnesium is observed to froth, indicating that a reaction is taking place. Some chemists claim that under these conditions the magnesium may ignite. I have not observed the slightest tendency in that direction. If perfectly dry chlorine is used instead, the frothing phenomenon does not occur. White anhydrous magnesium chloride is rapidly formed and a few sparks may indeed be observed during the process.

- Place aluminum powder in a bulb tube fitted with a ground-glass joint and prolonged by a long cooled tube. Some authors recommend using aluminum turnings rather than aluminum powder for this experiment. This precaution does not appear to be necessary. Heat the aluminum, but without bringing the glass tube itself to red heat, and then pass a stream of chlorine through the apparatus. Dense white fumes appear and the aluminum soon becomes incandescent, producing a brilliant white light, although less intense than that of magnesium burning in oxygen. This incandescence continues as long as aluminum remains and the chlorine stream is maintained. After cooling, purge the apparatus of any residual chlorine. A pale yellowish-white powder will be found deposited on the cooler walls of the tube.This powder is collected in water by immersing the tube in a large test tube containing water. A crackling sound is heard and fumes are evolved. Anhydrous aluminum chloride has thus been obtained, and the water has become charged with hydrochloric acid. For comparison, place a few drops of water on a small heap of commercial anhydrous aluminum chloride. Hydrogen chloride is evolved and insoluble aluminum hydroxide remains.

- In a refractory tube, place a thoroughly homogeneous mixture of alumina and powdered charcoal. Heat the mixture to red heat and then pass chlorine through the tube. A white powder is collected in a cooled receiver. This substance reacts vigorously with water and consists also of anhydrous aluminum chloride.

- If several pieces of nickel are placed in a tube and heated while dry chlorine is passed through it, the metal rapidly loses its metallic luster. A reaction therefore takes place, although it is not particularly vigorous.

- If a drop of mercury is introduced into a large bottle filled with chlorine and stirred within it, the metal quickly loses its luster and leaves filamentous trails behind it

owing to the formation of mercuric chloride.
There is, however, a more spectacular way to demonstrate the reaction between chlorine and mercury. A stream of chlorine is passed over an elongated porcelain boat containing a few drops of mercury previously heated to about 200°C. The boat itself is placed inside a tube made of boro 3.3 glass. A white flame appears at the surface of the mercury and highly toxic mercuric chloride is formed. Appropriate provisions must therefore be made for recovering the reaction products.

- Chlorine is passed through a tube made of boro 3.3 glass containing a piece of bismuth. Nothing happens at room temperature. Only moderate heating is required, however, for the bismuth to react and produce dense white fumes of bismuth chloride ($BiCl_3$).

- Pass a stream of thoroughly dry chlorine through a borosilicate glass tube containing a small quantity of titanium that is heated with a Meker burner or a powerful Bunsen burner. The tube is connected to a receiving flask, itself attached to a vent line leading outdoors or to an efficient extraction system. The titanium becomes incandescent while white fumes are evolved. If heating is discontinued and the tube and receiving flask are then opened to the air, dense white fumes continue to be produced for quite some time. Needless to say, these toxic fumes must be removed by an efficient ventilation system or, failing that, the experiment should be carried out outdoors.

- In a refractory alumina tube, place a homogeneous mixture of titanium dioxide and powdered carbon in equal proportions. Heat the mixture to red heat and then pass chlorine through the tube. This is a classical experiment described in various chemistry manuals and is intended to yield, in a well-cooled receiver, liquid titanium tetrachloride ($TiCl_4$), a colorless liquid that fumes in air and dissolves in water. As often happens, however, the actual results may vary considerably depending on several factors. Thus, in his *Dictionnaire de Chimie*, Wurtz already noted that the liquid may appear yellow owing to dissolved chlorine. I have also observed the formation of an abundant yellow powder that does not appear when chlorine is replaced by air or when the experiment is repeated without the addition of carbon. This yellow powder appears to be an oxychloride of a type that has received little study. If a hydrochloric solution of titanium tetrachloride is prepared and zinc is added, the solution develops a violet coloration.

- Place a small quantity of cobalt powder in a tube made of boro 3.3 glass and pass through it chlorine that has been dried by passage through a calcium chloride tube. When the tube containing the cobalt becomes yellowish-green owing to the presence of chlorine, begin heating the portion containing the metal. At a certain temperature, a glowing red spot appears. It soon spreads throughout the entire metallic mass while only faintly colored fumes are evolved (Figure 103). When the incandescence ceases, stop the experiment and allow the tube to cool. It is then found to contain a blue-violet crystalline mass corresponding to anhydrous cobalt chloride. If the tube is left open in a humid place, the crystalline mass gradually

turns pink, a characteristic property of cobalt chloride, once used on small figurines that served as hygrometers.

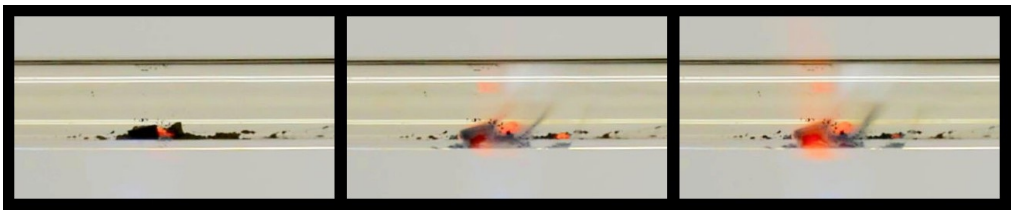


Figure 103

- If chlorine is passed through a borosilicate glass tube containing tungsten and the metal is heated, pale yellowish-white fumes appear. After cooling the tube, a little distilled water is introduced. A neutral, colorless liquid is obtained.

- If thoroughly dry chlorine is passed through a borosilicate glass tube containing molybdenum heated with a Meker burner, reddish-brown fumes rapidly appear. When heating is discontinued and the tube allowed to cool, a yellow substance is found where the metal had been, while the condensed fumes display shades ranging from red to emerald green. As soon as the tube has cooled, it is placed in a flask and distilled water is allowed to run over its inner walls. Ink-blue streaks immediately appear while fumes fill the flask. The resulting liquid is strongly acidic and produces a white precipitate with silver nitrate. This precipitate rapidly turns violet when exposed to sunlight. Nitric acid, hydrogen peroxide, or an aqueous solution of potassium thiocyanate quickly render the solution colorless. Hydrochloric acid and sulfuric acid produce the same effect, although more slowly.

- Finely divided vanadium, when heated in a stream of chlorine, rapidly becomes red-hot and gives off a cloud ranging in color from yellow to dark brown, corresponding to the formation of a tetrachloride. When the tube is rinsed with water, a beautiful blue solution is obtained, characteristic of the vanadyl cation VO^{++}. This solution turns yellow if a few drops of hydrogen peroxide or a solution of sodium hydroxide are added. If a little zinc powder is introduced into the same blue solution, it becomes yellow within a few tens of minutes. A slight precipitate is produced upon addition of potassium ferrocyanide solution.

- Arsenic powder projected into a large bottle filled with chlorine does burn, but far less spectacularly than most chemistry books would lead one to believe. In practice, all that is observed is the instantaneous formation of white fumes.

- Chemistry books often state that powdered antimony ignites or burns spontaneously when dropped into a flask of chlorine. In reality, although a reaction does occur, it is rather weak and produces only a small amount of white cloud.
To obtain actual combustion, the antimony must first be heated. Under these conditions, ignition and dense white fumes are evolved quite similar to that of powdered red phosphorus in chlorine (Figure 104).
One of the keys to the success of this experiment is the distance through which the

antimony falls while passing through the chlorine. The greater this distance, the greater the likelihood that the antimony will ignite. For this reason, either a long chlorine-filled tube or a very large bottle should be used. The Erlenmeyer flask shown in Illustration 104 had a capacity of six liters, which is not common in an amateur laboratory.

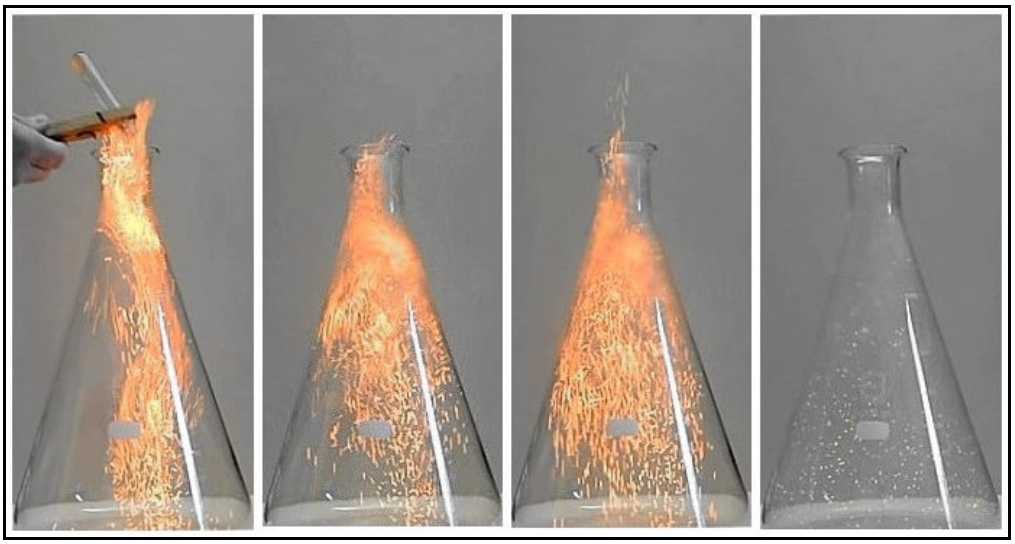


Figure 104

- When heated in a tube through which chlorine is passed, antimony reacts readily. Depending on the proportions of the reactants and the temperature employed, either antimony trichloride ($SbCl_3$), having a buttery consistency, or yellow liquid antimony pentachloride ($SbCl_5$) is formed. The latter may be collected in a receiver immersed in an ice-and-salt bath. This liquid decomposes immediately upon contact with water.

- Chlorine is passed through a tube made of boro 3.3 glass containing a piece of boron. Fairly strong heating (about 400°C) is then required before the reaction begins. The boron becomes incandescent and red fumes are observed, condensing into a yellow liquid (Figure 105).

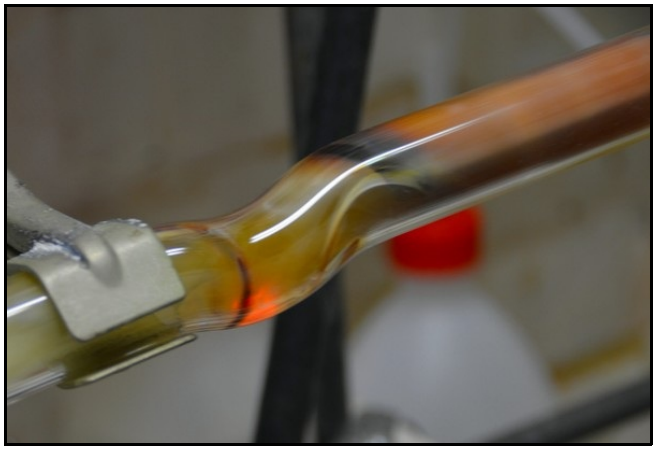


Figure 105

- Dry chlorine is passed over calcium oxide (quicklime) strongly heated in a bulb tube. After cooling, the product is transferred into a large test tube containing a few centimeters of water and allowed to settle. A few drops of silver nitrate solution are then added. A white precipitate that rapidly turns violet in sunlight demonstrates the formation of calcium chloride. During the experiment it may also be observed that oxygen is evolved from the outlet of the tube, since it

readily relights a glowing splint.

- The same experiment may be carried out with magnesium oxide. In that case, magnesium chloride is formed.

- Chromic anhydride is placed in a 100 mL cylindrical dropping funnel with the stopcock left open. The ground-glass outlet of the funnel is connected to a vertical condenser whose lower end leads to a small receiving flask, itself connected to a system for exhausting harmful gases. Through the upper opening of the funnel, and using only ground-glass connections, a stream of chlorine previously dried by passage over calcium chloride is introduced. As the chlorine passes through the apparatus, the funnel fills with a red gas that flows downward together with a liquid. This liquid is chromyl chloride. This experiment is, however, less satisfactory than the corresponding preparation carried out with gaseous hydrogen chloride instead of chlorine, as described later.

- Pass gaseous chlorine over a small amount of potassium ferrocyanide gently heated. It is converted into potassium ferricyanide.

- Chlorine is passed over iron sulfide strongly heated in a tube made of boro 3.3 glass or silica. A red-and-yellow cloud appears. At the outlet of the tube, a condensation flask cooled by running water or ice is provided. The experiment is not continued for very long, after which the entire apparatus is allowed to cool. A yellow flow, a red-yellow deposit, and small shining crystals may then be observed inside the tube. The remaining fragments of iron sulfide are removed and placed in a small quantity of water. Addition of ammonia solution or sodium hydroxide solution produces a green precipitate of iron(II) hydroxide. A little water is then allowed to run over the walls of the tube, and the yellow liquid obtained is collected. Addition of ammonia solution or sodium hydroxide solution now produces a brick-red precipitate of iron(III) hydroxide. Both iron(II) chloride and iron(III) chloride have therefore been formed. The pestilential odor and the slight evolution of fumes from the cooled receiver indicate that sulfur chloride has also been produced.

- Mercurammonium chloride is first prepared by adding an excess of ammonia solution to an aqueous solution of mercury(II) chloride. The precipitate is allowed to settle and the excess liquid is decanted. The solid is filtered through fine filter paper and washed with distilled water in order to remove part of the ammonia. The filter paper is then cut so as to retain only the portion containing the precipitate. This paper is placed in a large bottle into which chlorine gas is introduced. At first, white fumes of ammonium chloride may occasionally be evolved. Subsequently, the precipitate becomes warm and liquefies. I was unable to observe the ignition reported by certain authors.

- Pass a stream of chlorine through a tube containing calcium carbide while heating the latter. At a certain point, a glowing red spot appears on the carbide and gradually spreads through the mass. The apparatus is then allowed to cool. The material has

become black. When thrown into water, it no longer reacts. It has been converted into carbon. Other authors state that calcium may be produced under these conditions, in which case it would obviously react with water. I have not observed this.
NOTE: Because the temperature becomes extremely high in a localized region of the tube, the latter may crack during cooling. In any event, the glass is damaged, and it is therefore preferable to use a tube that can be sacrificed if necessary.

- Pass thoroughly dry chlorine through a two-neck flask containing 50 g of urea and immersed in an oil bath maintained at 140°C, a temperature slightly above the melting point of urea. Various products are formed, including hydrogen chloride, nitrogen, ammonium chloride, and cyanuric acid. The first two may escape through the second neck of the flask. After cooling, dissolve the ammonium chloride in water. Boil the remaining material and then allow it to crystallize. The product obtained is cyanuric acid, which is only sparingly soluble in cold water.

- Place a small quantity of crystalline citric acid in a large bottle exposed to sunlight. Then pass a considerable stream of chlorine through the vessel. Often, nothing visible appears to happen, unless the solid acid, if initially well dehydrated, is transformed into an oily liquid. However, the addition of a little water to the bottle produces a strong insecticide-like odor.

- Place a small quantity of naphthalene in a U-tube and pass a stream of chlorine through it. Little by little, the naphthalene liquefies to form a thick yellowish oil that is soluble in ether. It is sometimes necessary to warm the naphthalene very gently in order to initiate the reaction.

10.2.1 Chlorine Dioxyde (ClO_2)

Chlorine dioxide is a highly toxic and explosive gas that is extremely dangerous both to produce and to handle (see the remarks made on pages 93).

Figure 106

- One of the simplest ways to appreciate the hazards associated with this gas is the following. Outdoors, on a flat concrete surface, place a tall-form beaker of 300 to 500 mL capacity whose bottom has been covered with a thin layer (3mm) of potassium chlorate. Suspend, by means of a string, a small porcelain boat containing a quantity of sulfur about the size of a small pea so that it hangs approximately halfway up inside the beaker. Pour in, all at once, a small quantity of concentrated sulfuric acid sufficient to cover the bottom of the vessel, then move away immediately. The potassium chlorate instantly turns red while the beaker begins to fill with a greenish gas (Figure 106). As soon as this gas reaches the sulfur, sharp detonations are heard, somewhat resembling loud crackling sounds,

and fragments of sulfur are expelled from the beaker. In contact with sulfur (as well as with phosphorus or arsenic), chlorine dioxide reacts explosively. Figure 106 gives an idea of the violence of the reaction: solid fragments may be seen scattered across the ground, while liquid projections are visible on the dark surface in front of the beaker. The toxic gaseous cloud is still clearly apparent. It is necessary to remain well away from the vessel for quite some time, since detonations and projections may continue for an extended period. When no further detonations have occurred for several minutes, jets of water should be directed into the beaker with a wash bottle while maintaining a safe distance. New detonations and projections then recommence with renewed intensity. Only gradually, as more water is added, does the danger diminish and eventually disappear.

10.3 HCl

- A long porcelain boat containing a thin layer of iron powder is placed inside a porcelain or alumina tube. The boat is pushed into position with the aid of a glass stirring rod. The tube is heated to red heat in the region of the boat, after which a stream of hydrogen chloride dried over concentrated sulfuric acid is passed through it. After cooling, the layer formed on the iron is dissolved in boiled water. Tests with ammonia solution, sodium hydroxide solution, and potassium ferrocyanide solution show the same precipitates as those obtained from ferrous chloride.

- Gaseous hydrogen chloride is passed over pieces of nickel heated in the middle of a long porcelain tube. Some European demonetized coins cut into small pieces are often well suited to this purpose, since they are made of nearly pure nickel. The metal becomes coated with yellow anhydrous nickel chloride, which may subsequently be dissolved in water.

- Chromic anhydride is placed in a vertical tube fitted at its upper end with a ground-glass joint and connected to a condenser. The chromic anhydride is supported by a light plastic mesh. The upper part of the tube is connected to a hydrogen chloride generator, the gas being dried before entering the apparatus.
At room temperature, although preferably with gentle warming of the tube, red vapors are formed. These are collected, much as in a distillation, as a dark red liquid. This liquid is chromyl chloride.
WARNING: all apparatus and joints must be made of ground glass and/or PTFE, since chromyl chloride attacks rubber as well as many other materials. Provision must also be made for safely exhausting excess harmful gases.

- The following arrangement is assembled. At its center is placed a refractory tube at least 40 cm long containing green chromium oxide. At one end of the tube, a mixture of air (supplied by an aquarium pump) and gaseous hydrogen chloride is introduced. At the other end, a Drechsel bottle containing water colored with a dye that is not decolorized by hydrogen chloride but is decolorized by chlorine is

installed. The tube is first heated to red heat in the region containing the chromium oxide. Once the tube has reached red heat, the hydrogen chloride generator and the air pump are started simultaneously. The colored solution in the Drechsel bottle is soon decolorized, demonstrating the formation of chlorine.

- Pass thoroughly dry hydrogen chloride through a heated bulb tube containing cobalt chloride. A dramatic color change is observed.

- Copper(II) chloride crystals are placed in a U-tube immersed in an ice-water bath. A stream of thoroughly dry hydrogen chloride is then passed through the tube. The salt turns green and garnet-colored patches appear, consisting of cupritrichlorhydric acid.

- Place dry copper(II) chloride in a tube similar to a bulb tube. By bubbling air through a bottle containing concentrated hydrochloric acid, a mixture of air and hydrogen chloride is passed through the tube. At the same time, the copper chloride is heated moderately, and the exiting gas is collected in a Drechsel bottle containing about 3 cm of water. The copper chloride becomes brown. After one or two minutes, the experiment is stopped and the tube allowed to cool. Two test tubes are then prepared, each containing a little ordinary blue ink diluted with distilled water. One or two drops of concentrated hydrochloric acid are added to the first tube. The blue coloration becomes more intense. A small quantity of the water contained in the Drechsel bottle is added to the second tube. The ink is decolorized. Finally, some of the Drechsel water is added to the first test tube. This solution is likewise decolorized. The experiment thus demonstrates the formation of chlorine, which has dissolved in the water of the Drechsel bottle and may also be recognized by its characteristic odor.

- A yellow precipitate of neutral lead chromate is prepared by reacting an aqueous solution of lead acetate with an aqueous solution of potassium chromate. The precipitate is washed with water. If the moist yellow lead chromate is spread over the inner walls of a bulb and gaseous hydrogen chloride is then passed through it, a green liquid appears. This liquid is believed to be chlorochromic acid.

- Pass hydrogen chloride gas over urea placed in a U-tube (care must be taken not to block the tube). The urea liquefies, forming urea hydrochloride. A noticeable evolution of heat occurs. This substance decomposes in water, regenerating hydrochloric acid.

- Pass a large quantity of dry hydrogen chloride over natural camphor. Little by little, the camphor is transformed into a yellowish oil. Any remaining pieces of camphor are removed, and the hydrogen chloride is then completely expelled. Water is added. Hydrogen chloride is re-formed (verify that the liquid is acidic and gives a white precipitate that darkens in sunlight with silver nitrate), together with camphor, which is almost insoluble in water but highly soluble in alcohol.

10.4 SO_2

- A refractory tube containing sodium chloride is heated to red heat. Sulfur dioxide is first passed through a small flask containing water maintained at approximately 80 °C so that the gas becomes charged with water vapor. The moist sulfur dioxide is then passed through the hot tube. The gases leaving the refractory tube are in turn bubbled through water maintained at room temperature. When tested afterward, this water is found to be strongly acidic and reacts with silver nitrate to form a white precipitate that darkens in sunlight. Either chlorine or hydrogen chloride has been formed, depending on the temperature and on the gas-to-water ratio within the tube. It should be noted that the liquid also contains unreacted sulfur dioxide. If poured onto iron or zinc powder, it becomes yellow. After the tube has cooled, its contents are dissolved in water. This solution produces a white precipitate with barium chloride solution, indicating that sodium sulfate has been formed, albeit incompletely, in place of the original sodium chloride. The experiment is difficult to perform and not particularly demonstrative.

- Pass sulfur dioxide over iron powder heated in a silica tube. Green ferrous sulfate is formed first, followed by black iron sulfide. This may be verified by treating the product with hydrochloric acid, which liberates hydrogen sulfide. The latter may be identified with moist lead acetate paper, which turns black. At the moment when the iron begins reacting with sulfur dioxide, a small flash or a few sparks may sometimes be observed.

- Place a little zinc powder in one test tube, a little iron powder in a second, and a little copper powder in a third. Prepare a solution of sulfur dioxide in ethyl alcohol and fill each tube to about one-third of its volume with this solution. The tubes are then tightly stoppered and shaken from time to time. Only one or two hours are required before a white substance appears in the tube containing zinc. At least ten hours are needed before the tube containing iron develops a yellow coloration that gradually turns brown. More time still is required before the tube containing copper acquires a faint blue coloration. In each case, a dithionite of the type ZnS_2O_4, derived from dithionous acid ($H_2S_2O_4$), has been formed. Each of these compounds produces differently colored precipitates when treated with solutions of sodium hydroxide, ammonia, potassium ferrocyanide, potassium chromate, or potassium thiocyanate.

- Place some zinc powder and water in a Drechsel bottle standing on a magnetic stirrer. A stream of sulfur dioxide is then passed through the liquid. The solution gradually becomes yellow while warming noticeably. Zinc hyposulfite is formed (thiosulfateis in modern nomenclature), and sulfur may also be deposited. This yellow solution is a powerful bleaching agent that instantly decolorizes solutions of methyl orange, fuchsin, Congo red, and similar dyes. If an excess of ammonia is passed into this liquid, it turns white and deposits a white powder.

- Since sulfur dioxide is heavier than air, a large bottle may be filled with it simply

by displacement of air. A burning magnesium ribbon is then introduced into the bottle. Combustion continues and becomes dazzling, much as it does in oxygen. While the bottle fills with white fumes, yellow deposits of sulfur appear on its walls (Figure 107). The bottle is then stoppered and the fumes are allowed time to condense on the walls as a white powder. Afterward, the bottle is thoroughly ventilated and a small quantity of water is introduced and rinsed over the entire inner surface. The resulting liquid proves to be alkaline. Had the bottle not been aired beforehand, any remaining sulfur dioxide would have dissolved to form sulfurous acid, which could have neutralized the magnesium hydroxide produced and thus distorted the outcome of the experiment. This point rarely concerns the authors of chemistry books and illustrates the type of imprecision that may mislead experimenters, sometimes leading them to results completely at odds with those described in the literature.

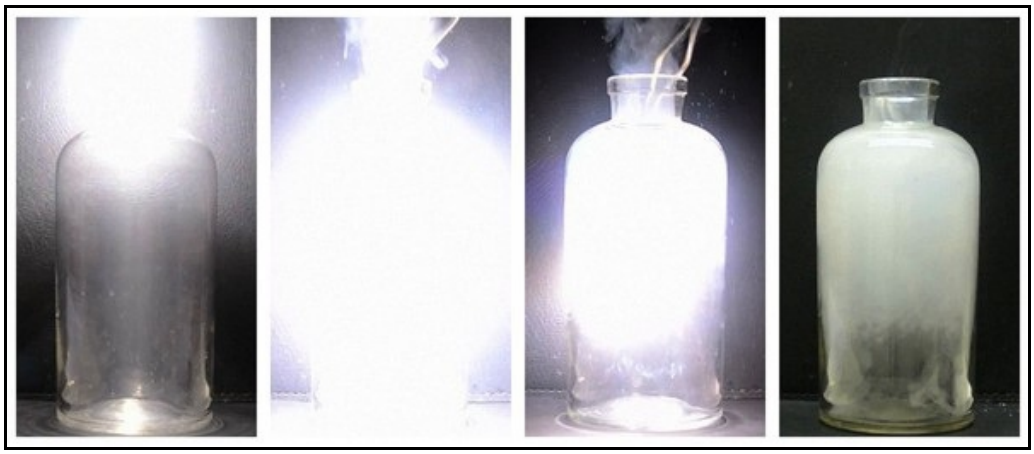


Figure 107

Figure 108

- Place a concentrated aqueous solution of sulfur dioxide together with a piece of nickel in a stoppered bottle fitted with a ground-glass stopper. Very gradually, the solution turns green owing to the formation of nickel sulfite and nickel hyposulfite. If the nickel was originally bright, it first becomes covered with a bluish-white layer and then, over the course of several days, with a black coating that detaches itself in small flakes when the bottle is shaken. The experiment must be allowed to proceed for at least a week in order to obtain a distinctly green coloration (Figure 108).

- Pass sulfur dioxide over tin heated to its melting point. The metal first becomes black and then solidifies. If the resulting material is subsequently treated with hydrochloric acid, it produces hydrogen sulfide, readily identified either by its odor or with filter paper moistened with lead acetate solution. A sulfide has therefore been formed.

- Pass sulfur dioxide over carbon heated to red heat in a refractory tube. The gas leaving the tube is then passed into limewater. The formation of sulfur and carbon dioxide may thus be demonstrated.

- Add a teaspoonful of manganese dioxide to 100 mL of an aqueous sulfur dioxide solution. Shake and allow the mixture to stand overnight. When the bottle is opened, the odor of sulfur dioxide has disappeared and the black powder has become brown.

- Pass sulfur dioxide through a tube made of boro 3.3 glass containing brown lead dioxide (PbO_2), and heat the tube. The oxide becomes incandescent and is converted into white lead sulfate.

- A Drechsel bottle containing water and nickel carbonate is placed on a magnetic stirrer. Sulfur dioxide, previously washed through a small quantity of water, is bubbled through the liquid. Very slowly, the initially opaque suspension clears and acquires a pale green coloration.

- Large crystals of sodium carbonate are placed in a bulb tube through which sulfur dioxide is passed. The crystals gradually dissolve in their water of crystallization to form a colorless liquid. After some time, small bubbles of carbon dioxide begin to emerge from the crystals and the transparent liquid is progressively converted into a white solid. If this solid is subsequently treated with concentrated sulfuric acid, sulfur dioxide is evolved. Acid sodium bisulfite or sodium hydrogenosulfite ($NaHSO_3$) has in fact been formed.

- Pass sulfur dioxide through a tube containing calcium carbonate while heating the latter. Sulfur, carbon dioxide, and calcium sulfate are formed.

- Pass sulfur dioxide through a tube containing heated barium peroxide. Incandescence accompanied by a surface flame is observed. The heat evolved by the reaction is often so intense that the tube breaks during cooling.

- Pass sulfur dioxide over manganese dioxide heated to red heat in a tube. The contents of the tube are then dissolved in water, allowed to settle or filtered, and treated with a little barium chloride solution. A white precipitate of barium sulfate is obtained. The filtrate reacts with sodium hydroxide, potassium ferrocyanide, and other reagents because manganese sulfate has been formed.

- The following apparatus is assembled. On one side is a sulfur dioxide generator. On the other is an air pump, such as an aquarium pump, whose airflow is passed through a Drechsel bottle containing water heated to at least 60°C so that the exiting air becomes charged with moisture. The sulfur dioxide and the moist air are then introduced together, by means of a Y-shaped connector, into a bulb tube containing medium-sized sodium chloride crystals. At the outlet, the bulb tube is connected by flexible tubing to a Drechsel bottle containing a small quantity of water colored red with Congo red. The air pump and the sulfur dioxide generator are started, and the

sodium chloride in the bulb tube is gradually heated with a Bunsen burner. The colored solution soon changes from red to blue. The experiment is then stopped and the blue liquid tested with silver nitrate solution. A white precipitate is obtained. Hydrogen chloride and sodium sulfate have in fact been formed within the bulb tube.

- Flowers of various colors are placed in a large closed jar into which sulfur dioxide is introduced. Most of the flowers become bleached. In some cases, the original colors gradually return after prolonged standing or after immersion in a dilute ammonia solution

10.5 NH_3

- In a tube made of boro 3.3 glass, sodium is heated until it begins to melt. A stream of thoroughly dry ammonia is then passed over it. White fumes appear, followed by the formation of a green layer of sodium amide. The metal subsequently ignites. The tube is usually lost because it shatters during cooling.

- In a boro 3.3 glass tube, or better still in a silica tube, strongly heat one piece of copper wire and another of iron wire, separated by at least one centimeter. Then pass a steady stream of perfectly dry ammonia through the tube. A change in the color of both metals is observed owing to the formation of unstable copper and iron nitrides.

- Place pieces of copper in an elongated glass bulb and completely cover them with concentrated ammonia solution. A steady stream of air is then introduced from below for at least one hour. This airflow may be supplied by a small compressor or, if the bulb is small, by an aquarium pump. The liquid gradually turns blue and eventually acquires a beautiful deep-blue color. It has been transformed into what is known as Schweitzer's reagent, which is reputed to dissolve cotton, linen, and cellulose. In practice, however, the action of this liquid on such materials is often disappointing (see the discussion in Chapter 12.3 concerning cuprammonium solutions and Schweitzer's reagent). During the experiment, frost will be observed forming on the outside walls of the bulb. Some authors recommend adding a little ammonium chloride to accelerate the process, but this does not appear to be necessary.

- Carbon is placed in a porcelain tube and heated to red heat before a stream of thoroughly dry ammonia is passed through it. The tube should be long and well cooled at its far end, or alternatively prolonged by a glass condenser. After one or two minutes, heating is discontinued and the apparatus is allowed to cool. The tubes are then rinsed with distilled water and the washings tested with a solution of picric acid. The solution first becomes more intensely yellow and, upon heating, gradually shifts toward red, indicating the presence of ammonium cyanide. The experiment

is difficult to conduct successfully, and the cyanide is not easily detected. Intense heating, preferably supplied by a row of burners, is required.

Pass dry ammonia through a moderately heated glass tube containing a small quantity of copper(II) oxide. Water vapor and nitrogen are evolved, while red copper powder remains in the tube. The temperature should not be raised excessively because, on the one hand, a detonating nitride might be formed and, on the other hand, the tube would become permanently stained red.

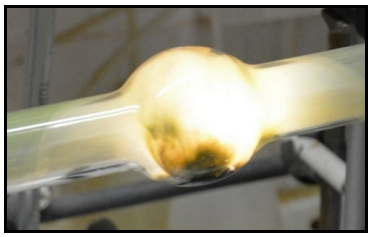


Figure 109

Thoroughly dry ammonia, previously passed through a column of quicklime, is introduced into a bulb tube containing chromic anhydride (CrO_3) heated moderately. A red glow first appears, followed by a large luminous flame (Figure 109), while green chromium(III) oxide Cr_2O_3 is deposited on the cooler walls of the tube. A related experiment may be carried out in the cold. A vertically mounted funnel fitted with a fritted-glass disc is used, and chromic anhydride is spread over the disc. Thoroughly dry ammonia is then introduced through the usual outlet tube. The anhydride gradually turns yellow and may occasionally ignite, leaving behind a grayish-green powdery residue.
For the same reaction carried out in the liquid phase, see pages 193-194.

- A 4- to 5-liter Erlenmeyer flask is charged with a small quantity of highly concentrated ammonia solution and covered with a watch glass. The bottom of the bottle is warmed gently with the palm of the hand in order to fill the vessel with ammonia gas. A small quantity of powdered green chromium oxide Cr_2O_3 is then heated in a short test tube until the glass becomes red-hot. With a rapid movement, the Erlenmeyer flask is uncovered and the hot oxide is poured into its neck. Immediately, what appears to be a miniature fireworks display of swirling red sparks is produced, some of them even emerging from the bottle. A slight white fume fills the vessel and, for several tens of seconds, tiny red sparks may continue to whirl about inside it (Figure 110).

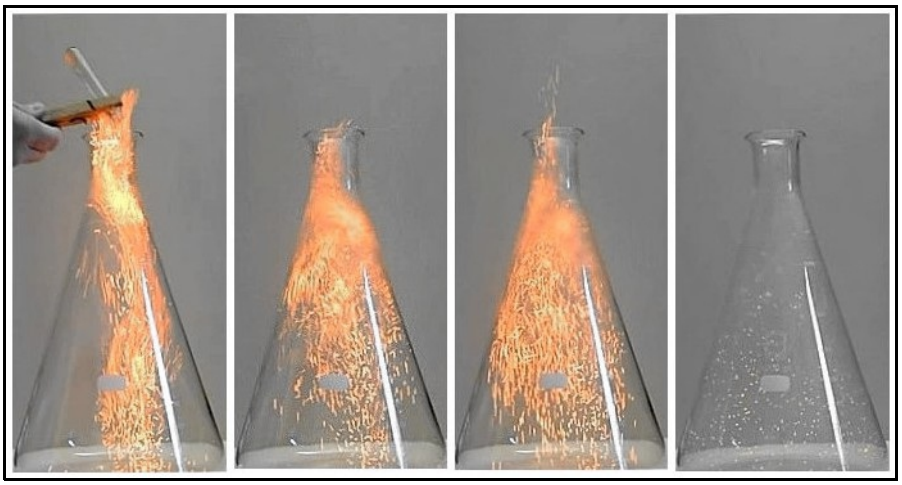


Figure 110

- Pass slightly moist ammonia over thoroughly dried calcium chloride. The calcium chloride rapidly "melts," forming an ammoniacal compound that may subsequently be decomposed by heat. For this reason, calcium chloride must never be used to dry ammonia gas.

- Copper sulfate is first heated in a glass test tube until it becomes completely white, that is to say, anhydrous. The salt is then spread in a glass tube through which a stream of dry ammonia is passed. It is useful to rotate the tube occasionally during the experiment. An indigo-blue compound is formed, accompanied by a considerable rise in temperature and an increase in volume. This compound dissolves in water and may even be fused in a test tube. In the latter case, water, ammonia, and ammonium sulfite are evolved, the latter condensing on the walls. The residue, initially black, becomes copper-red upon cooling. It consists of a mixture of copper and copper oxide that may be cleaned with nitric acid.

- Large crystals of nickel sulfate are heated in a test tube while the latter is rotated and maintained in a nearly horizontal position. The crystals become yellow while water vapor is evolved. Once all traces of water have been expelled, the crystals are transferred to a glass tube through which thoroughly dry ammonia is passed. The yellow crystals slowly become mauve-violet owing to the formation of an ammoniacal compound. Sometimes the color intensifies and spreads throughout the entire mass only after the experiment has been completed.
A somewhat similar experiment may be carried out in the liquid phase. Nickel sulfate crystals are dissolved in moderately concentrated ammonia, after which absolute alcohol is added. A different ammoniacal compound is then formed, this one being white. Upon standing, however, the deposit gradually becomes mauve, as in the gaseous-phase experiment.

- Pass thoroughly dried ammonia over nickel chloride spread as a very thin layer in a tube. The chloride, initially spring green, becomes spinach green, then blue, and finally white. When mixed with water, it gives a blue solution from which a pale green hydroxide slowly precipitates.

- Pass thoroughly dry ammonia over anhydrous aluminum chloride at room temperature. White swirls of fume appear and a considerable amount of heat is evolved. The substance liquefies and coats the glass, making cleaning difficult, though not impossible. Hydrochloric acid, nitric acid, or aqua regia may be used for this purpose.

- Spread a layer of cobalt chloride in a tube and pass thoroughly dry ammonia through it. The solid changes color, becomes pinkish white, and increases in volume. When poured into water, it yields a green solution while leaving behind cobalt oxide.

- Pass thoroughly dry ammonia over anhydrous manganese sulfate. After a few minutes, pour the solid into water. A yellowish precipitate of manganous oxide is formed.

- Pass dry ammonia over slightly heated mercury(II) chloride in a tube. The chloride appears to melt, and a white powder deposits in the cooler portion of the tube. When collected, this powder proves insoluble in water and turns yellow when boiled in it.

- At room temperature, thoroughly dry ammonia is passed over solid silver nitrate. The nitrate appears to melt immediately with considerable evolution of heat and is then transformed into a white powder. This powder subsequently dissolves in water, imparting a brown coloration to the liquid.

- Pass thoroughly dry ammonia over phenol. The phenol liquefies and becomes red, forming a coloring substance known as corallin. Wurtz, however, reported a blue coloration and recommended passing a strong current of air through concentrated ammonia before introducing it into the phenol flask without prior drying. I observed that, after liquefying and developing scattered red patches, the phenol remained liquid but did indeed slowly turn blue when exposed to sunlight—a "detail" that Wurtz did not mention, perhaps because many experiments in his day were performed in daylight rather than, as is often the case in modern laboratories, under artificial lighting.

10.6 CO and CO_2

WARNING

A mixture of carbon monoxide and air may explode when exposed to a flame or to sufficiently high temperatures. Great care must therefore be taken never to ignite carbon monoxide mixed with air and never to heat a tube through which carbon monoxide is passing unless all air has first been completely purged from the apparatus.

- Filter paper impregnated with gold chloride and placed in a stream of carbon monoxide develops a violet coloration.

- A strip of magnesium introduced into a bottle completely filled with carbon monoxide continues to burn, although less intensely than in air. This experiment should be attempted only by an experienced chemist. It is essential to ensure that the bottle contains pure carbon monoxide and not a mixture of carbon monoxide and air, since the burning magnesium could otherwise trigger an explosion. The bottle should therefore be filled completely over a water trough before being stoppered and placed in position. The stopper should be removed only at the very moment when the burning magnesium ribbon is introduced. It may also happen that the carbon monoxide itself begins to burn with a blue flame descending gradually

into the bottle. In such a case, it is best to stopper the bottle immediately in order to extinguish the combustion.

- A precipitate is prepared by adding sodium hydroxide solution to a solution of mercury(II) chloride. The precipitate is washed, dried, and heated until an orange mercuric oxide is obtained. This oxide is placed in a bulb tube through which a stream of carbon monoxide is passed. Once the tube has been completely purged of air, it is heated moderately. The oxide changes color and, beyond the bulb, a grayish film of minute mercury droplets appears.

- A continuous stream of carbon monoxide is passed through a tube made of boro 3.3 glass containing barium peroxide. At a certain point, incandescence occurs. The flame then diminishes, stabilizes, and continues until the entire mass has been transformed.

- A small quantity of Fe_2O_3 is placed in a tube made of boro 3.3 glass through which a stream of carbon monoxide is passed. Once the tube has been completely purged of air, the oxide is heated strongly. The gas leaving the tube is bubbled through limewater, which rapidly becomes cloudy owing to the formation of carbon dioxide from the reduction of the oxide. The original red oxide is thereby transformed into black iron powder.

- Pass carbon monoxide over manganese dioxide previously heated in a bulb tube. Care should be taken to ensure that all air has been purged before heating begins. The manganese dioxide is converted into manganese carbonate, which is gray while hot and becomes reddish on cooling.

- An tubulated bell jar having a diameter of approximately 10 to 12 cm is arranged so that its tubulure is in the lower position, allowing carbon dioxide to be introduced through it. A burning candle may be used to verify that the carbon dioxide gradually rises within the bell jar. A strip of burning magnesium, however, continues to burn in the region where the candle is extinguished. At the same time, carbon is liberated. If a tubulated bell jar is unavailable (it is a rather uncommon and expensive piece of glassware), a Woulff bottle or even a 1.5-liter mineral-water bottle cut at approximately four-fifths of its height may be used instead.

- Ignite a piece of sodium in a combustion spoon and introduce it into a tubulated bell jar filled with carbon dioxide from below. The sodium then burns without a visible flame, removing oxygen from the carbon dioxide and liberating carbon, which blackens the walls of the vessel.
The same experiment may also be performed in a tube made of boro 3.3 glass by heating sodium while passing a stream of carbon dioxide over it.

If titanium is heated in a tube made of boro 3.3 glass through which a stream of carbon dioxide is passed, the metal becomes incandescent and changes color. Upon cooling, it exhibits a range of colors extending from orange-yellow to ultramarine

blue (Figure 111).

Figure 111

- Pass a fairly strong stream of carbon dioxide through the bottom of a vertical tube containing very small pieces of white phosphorus supported on a loose plug of glass wool located about halfway up the tube. The upper end of the tube is closed with a stopper pierced by a small opening through which a drawn-out glass tube passes. If the carbon dioxide succeeds in carrying a small amount of phosphorus vapor outward, a green flame may appear at the tip of the drawn-out tube.

10.7 H_2S

- In a vertically held test tube containing copper powder, a stream of oxygen is first introduced. A puff of hydrogen sulfide is then admitted. The copper immediately blackens owing to the formation of copper sulfide.

- In a wide horizontal glass tube, place a small pile of copper powder and, several centimeters away, a second pile of iron powder. Using a small spray bottle, moisten both the tube and the powders. A stream of hydrogen sulfide is then passed through the tube. Both metals immediately blacken owing to the formation of sulfides at room temperature.
The same experiment may also be carried out by passing hydrogen sulfide that has been moistened by bubbling through cold water or, preferably, warm water.

- Pass hydrogen sulfide through a tube containing zinc powder. Once all air has been purged from the apparatus, heat the powder to above 100°C. Small ignition points appear here and there within the powder, which gradually changes in appearance. When subsequently treated with hydrochloric acid, the powder now evolves hydrogen sulfide. It has therefore been transformed, at least in part, into zinc sulfide. The same experiment may be performed with iron powder.

- Pass hydrogen sulfide over small pieces of nickel placed in a strongly heated silica tube. The nickel swells and becomes brittle.

- Place a small quantity of boron in a boro 3.3 glass tube at least 40 cm long and pass a stream of hydrogen sulfide through it. Once the apparatus has been completely purged of air, heat the boron to red heat. A white substance is observed to deposit near the end of the tube. This region may be cooled with a little ice if necessary. After cooling, pass a stream of chlorine through the same tube. White fumes then appear in the region where the white deposit had formed. Some chemists report that ignition may occur, although I have never observed it.

- Hydrogen sulfide is introduced into a test tube containing a small quantity of chromic anhydride CrO_3. The color of the solid gradually changes. In some cases, the reaction may become vigorous enough to produce incandescence.

- Hydrogen sulfide, previously dried over calcium chloride, is passed through a bulb tube containing chromic anhydride heated moderately. A red glow first appears, followed by a large luminous flame, while chromium sulfide, green chromium(III) oxide, and yellow sulfur are deposited on the cooler walls of the tube.

10.8 NO, NO_2, N_2O_3

- Nitric oxide is passed over copper powder heated gently in a glass tube. The powder, initially red, immediately turns black owing to the formation of copper oxide.

- Nitric oxide is passed through a tube containing zinc powder heated fairly strongly. Suddenly, the zinc produces a beautiful blue flame accompanied by abundant white fumes.

- Nitric oxide is passed through a tube made of boro 3.3 glass containing a piece of boron. Once the tube has been thoroughly purged of the red fumes initially produced, the boron is heated to red heat. Boron nitride and boric anhydride are then formed quietly. After cooling, the remaining solid is placed in a small boro 3.3 glass test tube. A pellet of potassium hydroxide and a very small quantity of water are added. The mixture is heated while a strip of moist pH paper is held near the mouth of the tube. The paper soon reveals the presence of an alkaline vapor caused by ammonia.

- Pass nitric oxide, or a mixture of nitric oxide and nitrogen dioxide, over bismuth heated in a bulb tube. The bismuth is converted into a yellow oxide that may easily be removed afterward by cleaning the bulb tube with concentrated nitric acid.

- Pass nitric oxide through a tube containing a small quantity of an alkali iodate. Heat the tube gently. A nitrite is formed, while iodine deposits on the walls of the tube as fine crystals.

- A mixture of NO and NO_2, yielding N_2O_3, is prepared by allowing concentrated sulfuric acid to fall dropwise into a solution of sodium nitrite. This gas mixture is allowed to flow by gravity into a large bottle. A small porcelain crucible containing a pea-sized piece of sodium previously heated strongly in a Bunsen flame is then suspended in the bottle by means of a copper wire. Moderate combustion of the sodium is observed.

- Using the same method, a bottle is filled with N_2O_3 and a burning magnesium ribbon is introduced into it. The magnesium continues to burn, producing white magnesium oxide that deposits on the walls of the bottle.

- Pass NO_2 or N_2O_3 over cobalt powder heated gently in a tube made of boro 3.3 glass. The cobalt becomes incandescent and remains so as long as gas continues to flow and the oxidation is not yet complete.

- Place a small quantity of mercury in a rather narrow Drechsel bottle so that the dip tube barely enters the liquid metal. A stream of N_2O_3, generated by the action of sulfuric acid on sodium nitrite, is then passed through the apparatus. The mercury becomes noticeably warm. After a few minutes, the experiment is stopped and the apparatus disconnected. Once the Drechsel bottle has been opened to the air, it is gradually tilted toward the horizontal while the mercury is rolled over its inner walls. The metal adheres to the glass and forms a continuous mirror-like film while red fumes are evolved. The excess mercury is poured out and water is then introduced into the bottle. The mercury film detaches itself from the walls and the metal recovers its usual appearance.

10.9 N_2O

- An aqueous solution of nitrous oxide attacks a magnesium ribbon very slightly, small bubbles gradually appearing on its surface.
The solution acts similarly upon zinc powder, which likewise begins to evolve bubbles after several hours.

- In a large test tube, solid sulfamic acid and concentrated nitric acid are heated together to generate nitrous oxide. Once gas evolution has begun and the test tube is known to be filled with N_2O, a wooden splint is ignited in the flame of a Bunsen burner and then blown out before being immediately introduced into the gas while still bearing a number of glowing points. The splint instantly reignites and burns in the nitrous oxide with a luminous flame, much as it would in oxygen. Very often, this experiment fails because the splint does not retain enough glowing regions. To ensure success, the splint may be prepared beforehand. A piece of porous wood is soaked for several hours in a solution of potassium nitrate and then allowed to dry completely. Such wood ignites readily and, when its flame is blown out, retains

numerous glowing points.

Into a wide-necked Erlenmeyer flask filled with nitrous oxide by heating sulfamic acid with concentrated nitric acid, introduce a previously ignited magnesium ribbon. The magnesium then burns with an even more brilliant flame, as though it had been introduced into oxygen (Figure 112).

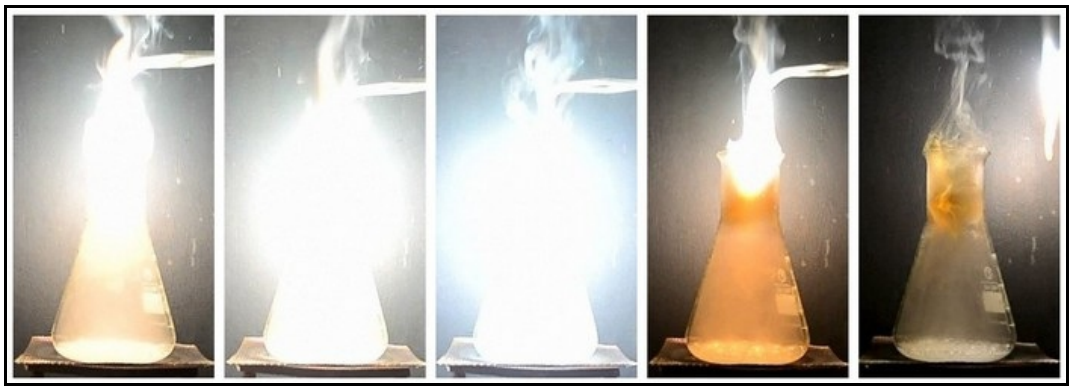


Figure 112

- Nitrous oxide, generated by heating sulfamic acid in concentrated nitric acid, is passed through a bulb tube containing iron powder or copper powder. In both cases, heating the powder to less than 200°C is sufficient to produce oxidation, revealed by blackening of the metal. The reaction is very distinct, although not particularly spectacular.

- The combustion of sulfur requires a considerably higher temperature and is more conveniently performed in a tube through which the gas is passed.

- The combustion of a piece of charcoal may also be attempted in the same gas and by the same method. The effect, however, is relatively unimpressive.

The combustion of phosphorus in nitrous oxide, on the other hand, is readily achieved and highly spectacular, following the same principle as the combustion of magnesium (Figure 113).

Figure 113

10.10 C_2H_2

- Acetylene is passed through a tube containing a piece of sodium and, once it has been established with certainty that all air has been purged from the apparatus (otherwise an explosion hazard exists), the metal is heated gently. The sodium then forms a glowing fire-red sphere (Figure 114) which, after cooling, appears black. Sodium acetylide has been formed. When moistened, it regenerates acetylene.
NOTE: Even when made of boro 3.3 glass, the tube is generally lost because it shatters during cooling owing to the intense thermal stresses concentrated in a small region of its surface.

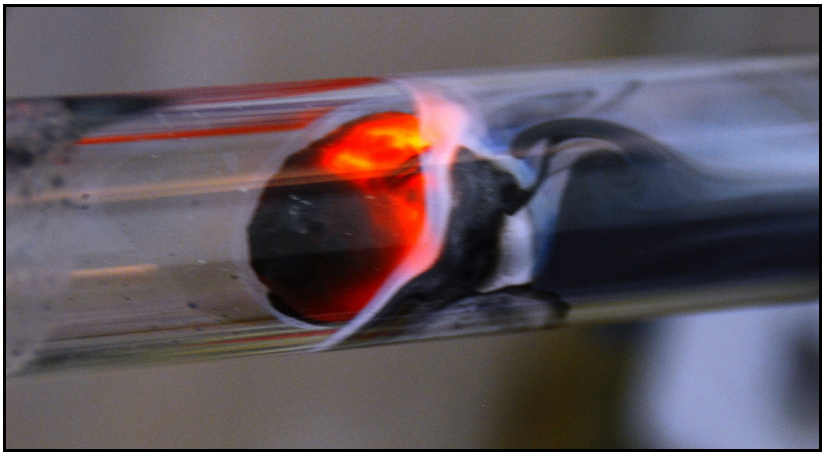


Figure 114

10.11 In Steam

- In a flask or Erlenmeyer flask, a small quantity of water is brought to a boil. A burning magnesium ribbon held with tongs continues to burn when introduced into the neck of the flask and brought into contact with the steam. If the white residue remaining at the end of the ribbon is mixed with a little cold water, the liquid becomes alkaline owing to the formation of magnesium hydroxide.

10.12 Aceton or Alcohol Vapors

- One cannot overlook the well-known experiment commonly referred to as the "flameless lamp." To perform it, a stemmed laboratory glass or a beaker is used, containing a shallow layer of alcohol or aceton. It is essential that the vapors of these substances completely fill the air space above the liquid. A fine spiral of copper (or, better still, platinum, although this is generally beyond the reach of the amateur chemist) is suspended from a piece of cardboard resting on the rim of the vessel. The cardboard should cover the vessel while still allowing gas exchange through a small notch. The spiral must approach the liquid closely without touching it. The spiral is first heated until red-hot and then placed in the vessel. It will remain incandescent

for as long as the air-vapor mixture is maintained under suitable conditions.
This is a delicate experiment that does not always work well. A number of conditions must be satisfied simultaneously, and it is sometimes necessary to vary the diameter of the spiral, the quantity of liquid, the shape of the vessel, its height, the temperature of the liquid, or the size of the notch. In short, numerous trials are often required, and success is never guaranteed, contrary to what some chemistry treatises might lead one to believe.

- By means of a small pump, air is passed through methyl alcohol and then through a refractory tube filled with pumice stone that is heated gradually. Beyond the tube, the gases are bubbled through a small quantity of water. When the refractory tube reaches red heat, faint muffled explosions are heard within it. The experiment is then stopped. Examination of the water shows that it has become charged with formaldehyde.

ANOTHER LITTLE-KNOWN "KIPP APPARATUS"

The name of the pharmacist Petrus Jacobus Kipp (1808–1864) is well known in chemistry because of the apparatus consisting of three superimposed bulbs that he invented to supply various gases on demand and at a steady rate (See chapter 4.1).

Kipp was also the inventor of another ingenious device that is rarely mentioned in the literature.

It consists of a special type of glass stopper fitted to a bottle, allowing an almost identical quantity of liquid to be dispensed each time by means of a few simple movements.

To use it, the bottle is simply tilted into a horizontal position. The liquid it contains then fills reservoir “R” through the opening indicated here by the arrows. When the bottle is returned to the upright position and then tilted slightly in the opposite direction, this quantity of liquid can be poured out through the spout. A second opening at the top of the outer sleeve allows the liquid to flow freely.

Chapter 11 – Liquefaction of a Gas

PRELIMINARY REMARKS

Liquefying a gas in an amateur or school laboratory is not an easy task. It generally requires the production of relatively large quantities of gas and therefore a generator of appropriate capacity. It also requires cooling equipment that is seldom available commercially.

A tubulated bell jar placed with its tubulure downward and fitted with a vertical serpentine tube passing through a stopper can serve as an excellent cooling apparatus when filled with a suitable refrigerating mixture. A custom-made coil condenser based on the same principle can be ordered from a glassblower, but a simple PVC container with its bottom removed may

Liquefaction of Sulfur Dioxide

Place a substantial quantity of sodium sulfite in a large Erlenmeyer flask (at least 1 L capacity) and add just enough water to thoroughly wet the solid without leaving an excessive amount of free liquid. Concentrated sulfuric acid is then allowed to enter through a dropping funnel fitted with a stopcock in order to generate a large volume of sulfur dioxide. After drying, the gas may be condensed to a liquid by means of strong cooling provided by a mixture of calcium chloride and crushed ice.
Passing a vigorous stream of air through the liquefied sulfur dioxide lowers its temperature still further and may, for example, be used to solidify mercury. The mercury is placed in a narrow test tube immersed in the liquid sulfur dioxide while the air stream is introduced through a dip tube.
Safety note: Sulfur dioxide is highly irritating to the eyes and respiratory system. Liquid sulfur dioxide can also cause severe cold burns. This experiment should be carried out only with efficient ventilation and suitable protective equipment.

Liquefaction of Nitrogen Dioxide

To prepare a large quantity of NO_2/N_2O_3 from sodium nitrite, concentrated sulfuric acid is allowed to react with the salt in a 1 L flask fitted with an acid funnel of at least 250 mL capacity. The gas is first passed through an ordinary water-cooled condenser and then through a long coil immersed in a mixture of crushed ice and calcium chloride. Under these conditions it condenses to a blue liquid. If this liquid is subsequently poured into ice-cold water, two layers may form: a yellow layer of nitric acid and a blue layer of nitrous acid. In some cases the yellow layer fails to appear and nitrogen dioxide is evolved instead.
The condensed liquid may also be poured into benzene that has been cooled as much as possible. The solution gradually develops a green coloration.
The same experiment may be repeated with nitrogen dioxide obtained from heated lead nitrate. The vessel used for the decomposition, preferably a large Pyrex test tube, can later be cleaned by soaking in water followed by treatment with aqua regia.
SAFETY NOTE: These extremely toxic gases are capable of causing severe and sometimes delayed lung injury. All operations involving them must be carried out outdoors or in a properly functioning fume hood.

AN IMPORTANT NOTE REGARDING THE FOLLOWING CHAPTERS

While it is relatively easy to maintain a clear and consistent structure when describing experiments involving simple substances such as metals, it becomes much more difficult to establish and preserve a single logical framework throughout chapters devoted to experiments involving far more complex materials, such as mineral salts.

Whenever possible, the author has therefore attempted to organize each group of experiments according to a coherent plan, bringing together experiments that are related by their similarities in appearance, behavior, or underlying chemistry.

12 Cold Reactions (Liquids + Solids or Liquids + Liquids)

12.1 Reactions Involving Metals or Metalloids

Sodium, Potassium and Calcium

HANDLING SODIUM

Sodium should never be touched with the fingers. Moisture from the skin may convert it into caustic soda and may even ignite it. Always handle sodium with perfectly dry wooden or metal tongs. Cutting is best carried out using a sharp ceramic blade or a PVC knife.

- Small pieces of sodium are placed in a tightly stoppered bottle containing carbon disulfide (CS_2), and the bottle is left in a cool, dark place. The sodium fragments gradually become coated with a black layer that can be detached by shaking, causing it to settle at the bottom of the bottle. The experiment is continued for many weeks in order to obtain a substantial quantity of this black material. The unreacted sodium is then removed, and the well-shaken liquid is divided as evenly as possible between two crystallizing dishes. As soon as the carbon disulfide has evaporated from the first dish, ethyl alcohol is poured over the residue. A red liquid is obtained. When the carbon disulfide has evaporated from the second dish, the residue is allowed to stand for a few minutes. The black particles are found to be strongly deliquescent and visibly absorb moisture from the atmosphere. They are then drowned in water, which immediately acquires a ruby-red coloration. This aqueous solution stains the skin intensely and should therefore be handled with care. Various acids, including hydrochloric acid, produce in this liquid a yellow-brown precipitate of C_3S_2. This precipitate is insoluble in carbon disulfide but dissolves unchanged in alkaline hydroxide solutions, restoring the characteristic red color.

- A large earthenware dish is filled with water and a small fragment of sodium is dropped onto the surface. The metal rapidly assumes the appearance of a bright white metallic sphere that moves about on the water while emitting a faint, continuous hissing sound and releasing a little vapor. This is in fact water vapor produced by the high temperature reached at the surface of the metal. If a drop of hydrochloric acid has previously been added to the water together with a suitable indicator such as bromothymol blue or methyl orange, the sodium leaves behind a colored trail corresponding to the formation of sodium hydroxide, which immediately dissolves in the water and rapidly neutralizes the acid.
CAUTION: The final stage of the experiment may be hazardous. The sodium globule tends to lodge against the side of the vessel before bursting. One should therefore remain at a safe distance to avoid projections. If the vessel were made of glass, it could itself crack or shatter owing to the intense local heating produced at that point.

- A large glass or even PVC tray is filled with water. A thick filter paper approximately 10 cm in diameter is floated on the surface. The paper quickly becomes saturated without sinking. A small piece of sodium is then placed on the paper. Because the paper prevents the metal from moving freely, the sodium ignites. A yellow flame is produced and sodium hydroxide is formed.
CAUTION: Toward the end of the experiment the sodium occasionally explodes, ejecting dangerous fragments. It may also happen that the filter paper becomes perforated after a few seconds, which can likewise cause the metal to burst. Always remain at a safe distance and wear at least safety glasses.

- A freshly cut piece of sodium is dropped into a test tube containing absolute ethyl alcohol. As the metal gradually disappears, numerous bubbles of hydrogen are evolved. When all the sodium has been consumed, a drop of the resulting liquid is added to a small quantity of water containing phenolphthalein. The indicator turns red. A more precise pH measurement reveals a strongly alkaline solution. Sodium ethoxide has been formed. This compound may be obtained as a yellow powder (which does not keep well) by evaporating the alcohol. It is usually stored in alcohol, although commercially available 21% solutions are of little practical value in an amateur laboratory.

POTASSIUM AND CALCIUM

Peroxides may slowly form on the surface of potassium during storage and can cause spontaneous explosions. It is therefore clear that this metal should be avoided in an amateur laboratory.

Calcium, for its part, offers little interest beyond demonstrating how it reacts with water to produce hydrogen. Considering both its cost and its tendency under certain conditions to ignite spontaneously, its purchase and storage can likewise be regarded as neither useful nor necessary in an amateur or school laboratory.

Iron

- When 48% hydrobromic acid is brought into contact with an iron or steel nail placed in a test tube, the liquid acquires an orange coloration, indicating the liberation of bromine.

- A little dilute hydrobromic acid is poured onto iron powder. Hydrogen is evolved. After dilution, the liquid gives a white precipitate with silver nitrate. This precipitate dissolves in ammonium hydroxide.

- A nail immersed in moderately concentrated hydrochloric or sulfuric acid evolves hydrogen and forms a chloride or sulfate that gradually colors the liquid. An interesting observation is that the carbon contained in the steel is released as fine black particles.

- A large iron nail, such as a masonry nail, suspended by a thin iron wire, is immersed completely in a test tube containing fuming nitric acid. Apparently nothing happens. The nail is then removed and immediately immersed to about four-fifths of its length in another test tube containing moderately concentrated nitric acid. Again, no visible reaction occurs. The head of the nail is then touched with a copper wire that has previously been cleaned with emery paper. An energetic reaction immediately begins, accompanied by the evolution of toxic red nitrous fumes. This experiment illustrates the complex phenomenon known as the passivity of iron.

- A stoppered bottle containing a concentrated solution of bromine water is charged with a generous excess of iron filings. The bottle is then placed on a magnetic stirrer. A color change occurs rapidly and the solution gradually becomes green. The liquid is then filtered to obtain a green solution of iron bromide. Any excess bromine may be removed by bringing the solution to a boil.

- A nail placed in a copper sulfate solution appears to rust rapidly. In reality, the brown layer that forms and detaches from the nail is not rust but metallic copper. At the same time, the original solution gradually changes color owing to the formation of green iron(II) sulfate, which slowly turns brownish-yellow on exposure to air as iron(III) compounds are formed.

- Into a large test tube (approximately 3 cm in diameter), pour about 5 cm of an aqueous solution of sodium thiocyanate. Then add, with thorough mixing, 1 mL of hydrogen peroxide and 1 mL of concentrated hydrochloric acid. Some foaming may occur. Agitate well to minimize continued gas evolution. A spiral of iron is then dropped into the tube. A striking blood-red stream develops from the metal and soon colors the entire liquid.

- A bed of iron filings is placed in a bottle fitted with a screw cap that is not completely tightened, since gas will be evolved during the reaction. The filings are

covered with acetic acid diluted by more than half. The bottle is then left undisturbed for many days until the liquid acquires a beautiful red coloration. Iron acetate has then formed. There is no advantage in attempting to concentrate it. The liquid may simply be decanted and stored as obtained, provided some of the iron remains undissolved.

- A solution of iron(III) chloride and iron filings are placed in a bottle closed with a screw cap that is not completely airtight. The mixture should be shaken two or three times daily and allowed to stand for several days. At a certain stage, after shaking, the contents settle rather rapidly. A clearer liquid remains above while a reddish-brown flocculent material settles to the bottom. When tested with a solution of sodium hydroxide, the supernatant liquid produces a green precipitate of iron(II) hydroxide. Iron indeed has the property of converting iron(III) salts into iron(II) salts. However, through reaction with the air contained in the bottle and with the water present in the solution, the iron(II) chloride gradually gives rise to a brown ferric oxychloride.

- In a test tube, iron powder is mixed with zinc powder and the mixture is covered with several centimeters of concentrated ammonia solution. Hydrogen is slowly evolved. After about twenty-four hours, the walls of the test tube are found to be covered with tiny white crystals.

Zinc

- A strip of zinc introduced into a test tube containing 48% hydrobromic acid reacts vigorously. Hydrogen is evolved, producing the characteristic "barking" sound when a flame is brought to the mouth of the tube. After dilution, the liquid gives a white precipitate with silver nitrate, and this precipitate dissolves in ammonium hydroxide.

- Zinc reacts similarly, though somewhat less vigorously, in a solution of hydriodic acid.

- A strip of zinc reacts readily with moderately concentrated hydrochloric or sulfuric acid. Hydrogen is evolved abundantly, but the liquid remains colorless.

- A few pieces of zinc are placed in concentrated nitric acid. The attack is rapid and accompanied by the evolution of abundant red nitrous fumes. When the reaction has ceased, the presence of ammonium ions in the liquid may be demonstrated using Nessler's reagent.

- An aqueous solution of sulfur dioxide is poured onto zinc powder in a bottle. The liquid soon acquires a yellow coloration owing to the formation of zinc hydrosulfite, or zinc dithionite. If a portion of this solution is added to copper sulfate, finely divided metallic copper is immediately precipitated. The same substance reduces

many heavy-metal salts and slowly decolorizes indigo.

- A little zinc or iron powder is added to a solution of selenious acid and the mixture is agitated. The liquid gradually becomes red as elemental selenium appears in place of the metal.

- Zinc is placed in formic acid. At room temperature the reaction is very weak. A slight warming, however, causes torrents of gas to be evolved. Zinc formate is produced, part of which is insoluble in the liquid.

- Zinc powder is placed in a solution of citric acid. The metal slowly dissolves with the evolution of bubbles. A solution of zinc citrate in citric acid is thus obtained or, if some zinc remains after a few days, a fairly concentrated citrate solution. Periodic agitation is recommended.

- Concentrated ammonia is poured onto zinc powder. After some time, the zinc acquires the appearance of a light, swollen mass. The mixture is agitated and left to stand. This operation is repeated over several days until practically no more bubbles are released during agitation. A complex compound is thus formed, formerly and incorrectly referred to as zinc ammonide. Early chemists therefore claimed that zinc was the only metal capable of dissolving in ammonia.

- Metallic zinc is capable of displacing many other metals from their salts, although the rate of reaction depends greatly upon temperature and concentration. For example, when a strip of zinc is immersed in a solution of mercury(II) chloride and the test tube is shaken, the entire liquid becomes gray owing to the appearance of innumerable tiny droplets of mercury. Likewise, if a strip of zinc is placed in a solution of cadmium chloride, it becomes swollen after about twenty-four hours. Cadmium has been deposited upon the zinc, while the solution now contains zinc chloride. If a strip of zinc is suspended by a thread in a bottle containing a concentrated solution of lead acetate, the metal gradually becomes covered with brilliant crystals of lead, which may be detached by shaking and allowed to fall to the bottom. Ultimately, the liquid contains zinc acetate. If, at the outset, thin zinc strips are arranged so as to resemble a trunk with branches, a brilliant crystalline growth is obtained that poetic chemists of former times called Diana's Tree. To prevent the formation of an insoluble basic salt or lead carbonate produced by atmospheric carbon dioxide—which would slow or even stop the reaction—it is advisable to add a little acetic acid to the original solution, a precaution that surprisingly few chemistry texts mention. A similar experiment may be performed using a hot aqueous solution of lead iodide. If a strip of zinc is placed in a solution containing a cadmium salt, cadmium gradually deposits upon the zinc. When detached from the metal and treated successively with hydrochloric acid and sodium sulfide, it yields a yellow precipitate of cadmium sulfide. If iron(III) chloride is agitated with zinc powder, it is converted into iron(II) chloride, a change that may be verified from the color of the hydroxide obtained upon addition of a sodium hydroxide solution. If a zinc strip is immersed in a hydrochloric solution of antimony chloride, the zinc is

attacked and chlorine is evolved. At the end of the reaction, a black powder remains. This powder is antimony.

- The following experiment, derived from one of the preceding ones, is particularly curious. A zinc strip is immersed in a solution of mercury(II) chloride acidified with hydrochloric acid. The acid removes the oxide coating from the zinc while the mercury salt forms an amalgam on the surface of the metal. After some time, when the strip has acquired a uniform gray appearance and hydrogen evolution has almost ceased, it is removed, rinsed, and transferred to dilute sulfuric acid. Nothing happens. If the strip is then touched beneath the surface of the liquid with a copper wire that has previously been cleaned with emery paper, hydrogen is evolved from the copper rather than from the zinc. This phenomenon represents another form of passivity, distinct from that previously described for iron.

- A strip of zinc is placed in a solution of ammonium molybdate. As the metal becomes coated with a black film, the liquid successively turns blue, then green, and finally black.

- A zinc strip placed in an aqueous solution of iron(III) chloride produces, within twenty-four hours, a brick-red precipitate. Some authors state that the iron(III) ion is merely reduced to iron(II). This, however, is not what I observed.

- A zinc strip partially immersed in hydrogen peroxide gradually becomes covered with a white oxide.

- Zinc powder is stirred for several minutes in very concentrated ammonia using a magnetic stirrer. After the mixture has been allowed to stand, the zinc powder is found to have changed in appearance and to have become swollen. The compound formerly called zinc ammonide has formed.

- A strip of zinc and some powdered sulfur are placed in a test tube, and a little hydrochloric acid is added. Hydrogen is evolved immediately, but before long the characteristic rotten-egg odor of hydrogen sulfide also becomes noticeable.

- A strip of zinc reacts slowly with an aqueous solution of chromic anhydride, producing green chromium(III) oxide, which gradually settles out.

- A large test tube is charged with a little zinc powder and then covered with tincture of iodine, that is, iodine dissolved in water containing a small quantity of potassium iodide. The iodine solution slowly loses its color, and a light, floating mass resembling a zinc amalgam appears.

Copper

- At room temperature, copper reacts with nitric acid, but the nature of the reaction

depends upon the concentration of the acid. For this reason, an acid having a specific gravity of about 1.2 is generally recommended when the objective is to obtain nitric oxide alone. At other concentrations, either nitrogen dioxide is formed directly, or a mixture of nitric oxide and nitrogen dioxide corresponding to dinitrogen trioxide.

- There is sometimes a tendency to believe that, at room temperature, copper reacts only with nitric acid. This is not true. In the presence of air and even such a weak acid as vinegar, a toxic copper acetate is gradually formed. For this reason, vinegar should never be stored or heated in a copper pitcher or copper cooking vessel. The following experiment illustrates the action of the same acid under different conditions. A piece of copper foil measuring approximately 1 cm^2 is placed in a test tube and covered with glacial acetic acid. Nothing happens. A little 100-volume hydrogen peroxide is then added and the tube is shaken. Within the vortex created by the agitation, a small blue spot becomes visible. Thereafter, the copper slowly becomes coated with blue copper acetate. Gentle warming greatly accelerates the formation of this compound.

- A short test tube fitted with a ground-glass stopper is charged with a strip of copper and concentrated hydrochloric acid. After a few hours, the portion of the copper exposed to the air above the liquid becomes coated with a colored film which, after a night, turns completely black. During the following day, this black layer gradually acquires a silvery appearance, while the liquid first becomes yellow, then green, and steadily darker. The reaction continues over the next several days until the upper portion of the copper has disappeared completely.

- It may also be observed that if a strong stream of air is passed through a hydrochloric acid solution containing copper, the liquid rather quickly develops a blue coloration.

- Copper turnings are placed in a bottle and covered with concentrated hydrochloric acid. Nothing happens. A little hydrogen peroxide is then added. The copper immediately turns black and the liquid becomes yellowish-green. Soon afterward, a greenish liquor begins to emerge from the copper. At first it spreads along the bottom of the bottle, then gradually diffuses throughout the liquid, while numerous bubbles begin to appear. A yellow-green gas (chlorine) soon fills the bottle, and the liquid becomes noticeably warm (Figure 115).

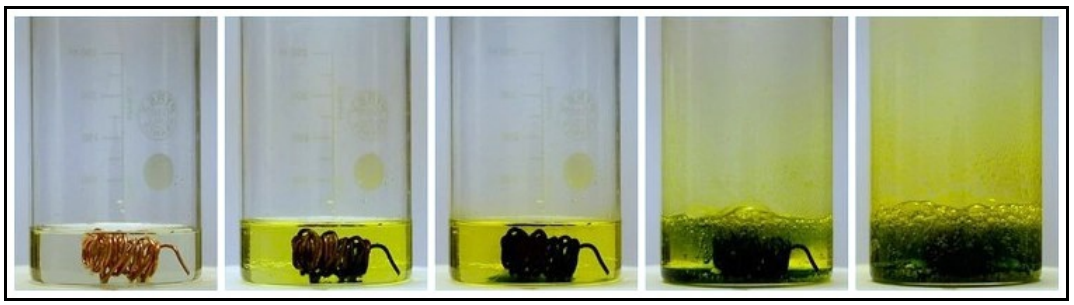


Figure 115

The bottle is then left either in the open air or under a fume hood until gas evolution has ceased. The liquid is then found to be a very dark yellowish-green, almost black. It is diluted with a large quantity of water until it assumes a pale green color, after which a solution of sodium hydroxide is added. A dirty yellow precipitate is obtained. This is allowed to settle and is then diluted with water. The liquid is stirred to distribute the precipitate uniformly and divided into two portions. To the first portion, a very small quantity of concentrated sulfuric acid is added. A beautiful blue-green liquid is obtained. The second portion is heated. The precipitate becomes brown. If a little sulfuric acid is then added and the mixture agitated, a white liquid is obtained which, upon standing, deposits a fine precipitate of the same color.

- Copper is attacked at room temperature by sulfuric acid provided that a few drops of hydrogen peroxide are added. A blue coloration then develops at the bottom of the test tube.

- The following experiment has already been mentioned on page 208 (Figure 97), but several variations may be described here. Place a strip of copper in a test tube containing dilute bromine water. Little by little, the original orange coloration changes to green. If bromine water saturated to the maximum extent is used instead (having remained in contact with an excess of bromine for several days), and pieces of copper are introduced before the vessel is tightly stoppered, the reaction proceeds differently. After many hours, the liquid changes successively from red-orange to brown, then to a raw-sienna yellow, then to emerald green, and finally to sky blue. A solution of copper bromide has formed. Evaporation under reduced pressure would yield crystals of copper bromide which, when heated, would release bromine and be converted into cuprous bromide.
Another way of carrying out the experiment is as follows. A little copper powder is sprinkled onto bromine contained in a small porcelain dish. A reaction occurs and the bromine gradually disappears. A black powder remains. When water is poured over it, a whitish coloration appears. Needless to say, this experiment should be performed outdoors or under very efficient ventilation.
Yet another variation may be used. Copper turnings are placed in a test tube and a few drops of bromine are added. Nothing happens. Water is then added and the contents are shaken. The water becomes greenish. After several hours, either a black, sticky liquid or a blue liquid is obtained, depending upon the proportions employed. If a black sticky liquid is present, additional water is added. A transformation occurs and the liquid becomes pale blue. Upon standing, an insoluble white powder settles while a beautiful cyan-blue solution remains above it. The black sticky liquid contains anhydrous copper(II) bromide. The white powder is cuprous bromide, which forms a deep ultramarine-blue complex in ammonia. The cyan-blue liquid is aqueous copper(II) bromide solution.

- Copper powder placed in a wide test tube and covered with tincture of iodine (water, iodine, and potassium iodide) slowly decolorizes the solution while various copper iodides are formed.

- A copper strip placed in an aqueous solution of mercury(II) chloride soon becomes covered with a white deposit that settles to the bottom of the tube within about twenty-four hours.

- A piece of copper tubing is placed in a test tube fitted with a ground-glass stopper and covered with a solution of yellow ammonium sulfide. The tube is tightly closed and left undisturbed for several days. The liquid gradually loses its color until it becomes completely colorless, while a layer of black copper sulfide detaches itself from the copper and falls to the bottom of the tube. Occasional shaking is beneficial. The presence of a small quantity of copper powder accelerates the reaction.

- Copper wire or copper turnings placed in a tightly stoppered bottle filled with an iron(III) chloride solution gradually develop a coloration whose exact shade depends upon the concentration of the salt and the quantity of copper employed. The liquid may tend toward either blue or green, owing to the simultaneous presence of blue copper(II) chloride and green iron(II) chloride. In some cases the solution first becomes cloudy, then deposits a brown flocculent precipitate, while the color continues to evolve for more than a week. The bottle should be shaken lightly each day.

- Two beakers are prepared, one containing sulfuric acid and the other a solution of sodium nitrite. A strip or some powder of copper is introduced into each beaker. Nothing happens. The contents of both beakers are then poured simultaneously into a larger vessel. Immediate and abundant foaming occurs, the liquid becomes blue, and a red gas is evolved which must not be inhaled.

- A shallow layer of silver nitrate solution is poured into a Petri dish. A copper wire is then arranged so that only a small portion of its surface is in contact with the liquid. After several hours, a circular growth of brilliant silver crystals has formed around the point of contact (Figure 116).

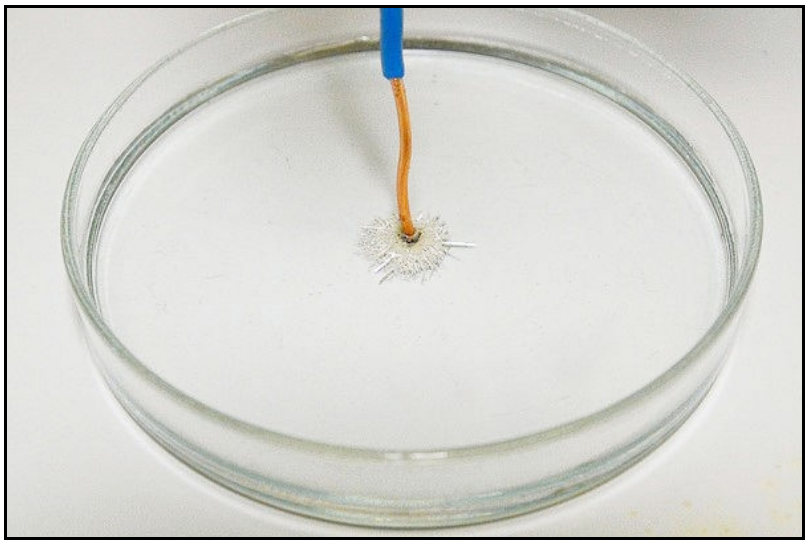


Figure 116

Similarly, if a copper strip is immersed in a silver nitrate solution, the copper soon becomes covered with delicate silver needles while the liquid turns blue owing to the formation of copper nitrate.

- Arsenic trioxide is mixed with hydrochloric acid diluted with an equal volume of water, and a broad strip of copper is placed in the resulting liquid. The copper gradually becomes black owing to the deposition of arsenic on its surface.

- The classical method of preparing copper sulfide consists of heating copper in sulfur vapors. The sulfide can, however, be obtained at room temperature. To do so, sulfur is first dissolved in carbon disulfide. A strip of copper or some copper powder is then introduced into the solution. The formation of black copper sulfide is observed quite rapidly.

Nickel

- Nickel is attacked at room temperature by sulfuric acid provided that a few drops of hydrogen peroxide are added. A green coloration then develops at the bottom of the test tube.

- Nickel reacts in the usual manner with hydrochloric and sulfuric acids at room temperature, although the reaction remains weak when these acids are dilute.

- Nickel reacts with fuming nitric acid in much the same way as iron, becoming passive. Another similarity with iron is that nickel is magnetic.

- A piece of nickel is introduced into a vertically positioned test tube, followed by a little water and finally a small quantity of bromine. The tube is closed with a stopper that can easily lift should excessive pressure develop. The reaction is slow to begin. It is sometimes necessary to wait a considerable time and then agitate the contents before the rather vigorous reaction starts. At the outset, it is advantageous to fill the tube with carbon dioxide in order to avoid a secondary reaction with the air.

- A nickel strip placed in an aqueous solution of mercury(II) chloride becomes coated within a few hours with a white deposit that subsequently falls to the bottom of the tube.

Tin

- Tin reacts with nitric acid, producing abundant red nitrous fumes while a white substance is deposited. This material dissolves in potassium hydroxide and is generally identified as metastannic acid.

- Some authors state that fuming nitric acid does not attack tin, but that the addition

of a little water causes the reaction to become highly exothermic and even luminous. I have never observed this luminosity.

- Excess tin is placed in concentrated hydrochloric acid. The attack begins slowly and gradually intensifies, accompanied by the evolution of hydrogen.To bring the reaction to a definitive end, the liquid is briefly boiled in order to drive off the small amount of hydrochloric acid that remains. For storage, the solution is allowed to settle and is poured directly into a bottle. A very small quantity of water may be added, although very dilute hydrochloric acid is preferable. If too much water is added, the salt decomposes.

- A small crucible is charged with a little bromine, after which two tin granules are dropped into it. The tin is rapidly attacked, producing red fumes and even a visible glow. At the end of the reaction, a clear liquid remains. This liquid may be diluted with water and consists of tin bromide ($SnBr_2$). This bromide reacts with manganese dioxide and sulfuric acid to regenerate bromine. Gentle warming may be required.

Lead

- Like tin, lead reacts readily at room temperature with concentrated nitric acid. Abundant red nitrous fumes are evolved, and a white substance is deposited. When heated, this material also produces red nitrous fumes.

Magnesium

- Magnesium reacts vigorously at room temperature with hydrochloric and sulfuric acids, even when these acids are dilute. It also reacts with many weak acids, including carbonated mineral water, owing to the presence of carbonic acid (H_2CO_3).

- Magnesium shavings are placed in a dilute (5%) aqueous solution of ammonium chloride. An immediate reaction occurs and numerous bubbles are evolved. An even more active system is obtained by adding 2% nickel chloride to the original solution. Magnesium behaves similarly in a solution of ammonium carbonate.

- Pour 5 to 6 cm of distilled water into a test tube at least 25 mm in diameter and add 3 or 4 drops of phenolphthalein solution. A strip of magnesium approximately 5 cm long is then introduced. Very quickly, the surface of the metal turns fuchsia owing to the formation of magnesium hydroxide (Figure 117). This is one reason why magnesium should be stored in a very dry atmosphere.

Figure 117

- Hydrogen peroxide is poured over magnesium granules. Gas evolution is observed and the granules slowly become coated with a white film. The liquid gradually becomes strongly alkaline. With 33% hydrogen peroxide, this reaction may continue for many hours.

- Magnesium turnings react strongly with brominated water. The bromine color gradually disappears while magnesium bromide is formed.

- A magnesium ribbon several centimeters long is placed in tincture of iodine (iodine dissolved in water containing potassium iodide). After many hours, the metal becomes coated with an orange film.

- About 5 mm of magnesium powder is placed in an ordinary test tube and covered with absolute alcohol. One or two large iodine crystals are then introduced. Before long, the liquid appears to boil. Hydrogen is evolved and may be recognized by the characteristic barking sound produced when a flame is brought near the mouth of the tube. The greenish liquid that remains contains magnesium ethoxide.

- Many chemistry texts state that magnesium is capable of displacing metals from the salts of iron, copper, cobalt, and nickel. For example, a magnesium ribbon immersed in a cobalt chloride solution becomes covered with a clearly visible green coating within about twenty-four hours. A magnesium ribbon immersed in a nickel sulfate solution causes the liquid to become cloudy within twenty-four hours, while a slight whitish deposit appears. The reaction is even more evident in a copper sulfate solution. After about twenty-four hours, a distinct deposit of red copper can be seen at the bottom of the test tube.

- If an excess of magnesium turnings is added to a fairly concentrated copper sulfate solution, an immediate reaction is observed. When it has ceased, a red copper powder is found at the bottom of the vessel. Hydrochloric acid is then added to dissolve the excess magnesium, after which the residue is washed several times with distilled water. The final product consists of copper in an extremely finely divided state.

- The behavior of magnesium in a lightly colored iron chloride solution is equally striking. Within the first few hours, a reddish flocculent deposit appears, part of which may even float. This deposit is not metallic iron, however, but more probably an oxychloride formed through contact with the air.

Aluminum

- Aluminum placed in a test tube containing hydrochloric acid undergoes a highly exothermic reaction that rapidly accelerates to such an extent that foam and liquid often overflow from the tube, while a jet of hydrogen can be seen piercing the foam at its summit. A similar reaction is obtained with formic acid.

- Hydrobromic acid reacts at room temperature with many metals, usually in a relatively gentle manner. With aluminum, however, the reaction is extremely vigorous. When 48% hydrobromic acid is brought into contact with a ball of aluminum foil, little or no reaction seems to occur at first. Then, quite suddenly, the reaction accelerates violently, liberating large quantities of hydrogen.

- A ball of aluminum reacts with an alkaline cyanide solution, although only very slowly.

- A small ball of aluminum foil is placed in each of two bottles, one containing limewater and the other baryta water. Gas evolution soon begins in the baryta water and much more slowly in the limewater. The aluminum disappears completely in the baryta water but merely blackens in the limewater. In both cases, aluminates are formed.

- A 500 mL three-neck flask is charged with tightly compressed balls of aluminum foil. About eight balls approximately 1 cm in diameter will suffice. Two dropping funnels are fitted to the side necks. One is filled with a sodium hydroxide solution and the other with a potassium nitrate solution. The central neck is fitted with a stopper carrying a delivery tube connected to a modified Drechsel bottle placed on a magnetic stirrer. The inlet tube of the Drechsel bottle should not dip into the water previously placed in it but should terminate about 2 cm above the liquid surface. Two or three drops of phenolphthalein are added to this water beforehand. The outlet of the Drechsel bottle is connected to a fume hood or other suitable gas-exhaust system. The sodium hydroxide solution is first allowed to flow onto the aluminum balls. Care should be taken not to add too much at once. Although the reaction is initially slow, it soon accelerates and becomes strongly exothermic. Along with hydrogen, sodium aluminate is formed. As soon as the reaction begins to accelerate noticeably, a small quantity of the potassium nitrate solution is introduced through the second dropping funnel. The water in the Drechsel bottle soon develops a beautiful coloration indicating a strongly alkaline pH. It may subsequently be verified that the water has absorbed ammonia gas, which is evolved in the presence of nascent hydrogen. It could be argued that the highly exothermic reaction might generate an aerosol of sodium hydroxide solution capable of reaching the Drechsel bottle and thus falsifying the results. This possibility may be eliminated by inserting a tube packed with glass wool between the reaction flask and the Drechsel bottle.

- A stoppered bottle is charged with carbon disulfide, iodine, and an excess of aluminum powder. The mixture is allowed to stand for a week or longer in a dark place. The contents are then poured into a crystallizing dish and exposed to bright sunlight or placed on a moderately warm surface in a well-ventilated location. The carbon disulfide evaporates and the remaining iodine sublimes. The residue is washed with water and filtered. An aluminum iodide solution is thus obtained. If a little manganese dioxide and a few drops of sulfuric acid are added, iodine is liberated again. Gentle warming may be required.

- A little mercury(II) chloride solution, which is only sparingly soluble, is placed in a test tube and covered with aluminum powder. If one places an ear near the mouth of the tube, gas evolution can be heard. An amalgam is formed which reacts with water to produce hydrogen.

- The following experiment, derived from the preceding one, is even more remarkable. A sheet of aluminum is immersed briefly in a mercury(II) chloride solution. It quickly loses its metallic luster. It is then rinsed rapidly under running water and transferred to a test tube filled with water. Small bubbles of hydrogen immediately begin to rise from the surface of the aluminum, which gradually disappears. Had the metal remained in the mercury(II) chloride solution, it would likewise have disappeared progressively.

- A little aluminum turnings are placed in an aqueous solution of green chromium sulfate. The solution is observed to turn blue gradually.

Chromium

- Chromium powder placed in a test tube containing hydrobromic acid reacts progressively at room temperature, producing within about half an hour a beautiful duck-egg-blue solution. Gentle heating subsequently accelerates the reaction.

- At room temperature, chromium placed in dilute hydrochloric acid rapidly evolves hydrogen while the liquid becomes azure blue owing to the formation of an aqueous solution of chromium(II) chloride. Gradually, however, if air is passed through the solution, the color changes to peacock green. If a strip of zinc is introduced into the final solution, it first reacts with the acid, producing an abundant evolution of hydrogen. At the same time, the liquid gradually changes color, becoming increasingly blue and even violet before eventually fading again upon exposure to air. The zinc strip itself becomes completely black.

Cobalt

- Cobalt reacts with dilute hydrochloric and sulfuric acids, evolving hydrogen and forming the corresponding salts.

- A little cobalt powder is added to dilute nitric acid in a test tube. The liquid becomes red. A cobalt salt is formed, ammonia is produced and combines with the acid, and nitrogen gas is evolved. If the experiment is performed with about 2 cm^3 of concentrated nitric acid and a little cobalt powder, a vigorous reaction occurs with the evolution of nitrogen dioxide.

- If cobalt is placed in fuming nitric acid, it becomes passive, like iron and nickel.

- Cobalt also reacts with hydrogen peroxide. Oxygen is evolved and an oxide is formed.

Cadmium

- A piece of cadmium placed in concentrated hydrochloric acid evolves hydrogen and forms cadmium chloride.

- A piece of cadmium is placed in dilute nitric acid. A vigorous reaction occurs, accompanied by the evolution of red nitrous fumes and the formation of cadmium nitrate.

- A piece of cadmium is placed in freshly prepared sulfurous acid. After about thirty minutes, a yellow mixture of cadmium sulfite and cadmium sulfide has already formed, without any noticeable gas evolution. The reaction should then be allowed to continue for several days.

- A piece of cadmium is placed in water saturated with bromine (not ordinary bromine water, which would be too dilute). The bottle is stoppered and left for a prolonged digestion period. After extended contact between the substances, white needles of cadmium bromide appear. These crystals are soluble in ether.

- A piece of cadmium, a little water, and some iodine are placed in a test tube that can be closed with a screw cap. The vessel is closed and left for several days, with occasional agitation. Eventually, every trace of iodine disappears and the liquid becomes completely colorless. The cadmium iodide formed remains dissolved in the liquid, a fact that can readily be demonstrated by adding a drop of hydrogen peroxide, which liberates iodine once again.

Manganese

- A piece of manganese immersed in hydrochloric acid evolves hydrogen very rapidly, a fact that can easily be demonstrated by bringing a lighted match near the mouth of the test tube.

- When immersed in concentrated nitric acid, a piece of electrolytic manganese immediately evolves nitrogen dioxide, which colors the liquid. With dilute nitric acid, the reaction is quite different. It is less vigorous, the liquid remains colorless, and various gases are evolved, including hydrogen.

- A piece of electrolytic manganese reacts only very weakly in concentrated sulfuric acid. In dilute sulfuric acid, however, it reacts vigorously while evolving hydrogen.

- At room temperature, a piece of electrolytic manganese rapidly causes the

decomposition of hydrogen peroxide with liberation of oxygen. After some time, the liquid acquires the characteristic pink coloration of manganese salts.

Boron

- A fragment of boron placed in a test tube containing hydrobromic acid reacts, particularly if the mixture is warmed slightly.

- A few milliliters of concentrated nitric acid are placed in a test tube, and a fragment of boron is added. The reaction is initially slow and may require a little heat. It then becomes progressively more vigorous. Red fumes escape from the tube and, ultimately, only a syrupy liquid containing a boron salt remains.

- A little crystalline boron is added to a silver nitrate solution. Metallic silver is gradually deposited.

- A little crystalline boron is added to a solution of a gold salt. Gold is gradually precipitated and the solution becomes colorless.

- A crystal of boron is placed in a lightly colored potassium permanganate solution. After a few hours, the solution becomes decolorized.

- A dilute iron(III) chloride solution is first prepared and verified to give a red precipitate with sodium hydroxide. If a little of this solution is placed in a test tube together with a fragment of boron, a color change becomes apparent after a few hours. The liquid now produces a green precipitate with sodium hydroxide solution. The iron(III) salt has thus been converted into an iron(II) salt.

Bismuth

- A piece of bismuth is placed in concentrated but non-fuming nitric acid. A vigorous reaction occurs. Nitric oxide is evolved and is converted into red nitrogen dioxide on contact with air. The liquid gradually acquires a green coloration due to dissolved nitrogen dioxide, which subsequently disappears, leaving a colorless solution of bismuth nitrate. Depending upon concentration, this solution may crystallize. If water is added, a white precipitate of basic nitrate appears. To avoid this hydrolysis, dilution should be carried out with water containing a little nitric acid. If nitric acid is poured back onto the precipitate and the mixture is agitated thoroughly, a clear solution is once again obtained.

- A piece of bismuth introduced into freshly prepared aqua regia reacts vigorously, forming a chloride that dissolves in the excess acid. Addition of water produces a white precipitate.

Vanadium

- Vanadium reacts at room temperature with nitric acid, even when the latter is slightly diluted. A beautiful azure-blue solution is obtained, accompanied by the evolution of red nitrous fumes. If hydrogen peroxide is added to this blue solution, a liquid of a beautiful red color is produced.

Molebdenum

- A little molybdenum powder is placed in a test tube and moderately concentrated nitric acid is added. A vigorous reaction occurs, accompanied by the evolution of nitrous fumes, and the contents of the tube gradually acquire a brick-red coloration. The mixture is then allowed to stand. After at least twenty-four hours, a very fine red precipitate covers the bottom of the test tube. This precipitate is washed and divided into two portions. A concentrated sodium hydroxide solution is added to one portion and concentrated nitric acid to the other. Nothing happens. If a little hydrogen peroxide is then added to each tube, a yellow solution is obtained in one and a red solution in the other.

- A little molybdenum powder is placed in chlorine water contained in a tightly stoppered bottle, which is then kept in the dark. Gradually, a beautiful blue solution is obtained. The odor of chlorine disappears, the liquid remains distinctly acidic, and it still produces the characteristic chloride precipitate with silver nitrate. When poured into water, the solution remains blue, although the color becomes lighter.

This blue solution gives a whole series of characteristic reactions, some of which are listed below.
Nitric acid or hydrochloric acid completely decolorizes it. The same effect is produced by a solution of sodium nitrite or sodium thiocyanate.
Aniline likewise destroys the blue coloration, the aniline collecting at the bottom of the vessel after agitation.
Hydrogen peroxide also decolorizes the solution, although a faint greenish tint remains.
Ammonia produces a similar effect, but the decolorization is not complete.
A solution of lead chloride in hydrochloric acid rapidly removes the blue coloration. Upon agitation, small white grains are precipitated. These dissolve when the liquid is heated and reappear upon cooling.
Potassium ferrocyanide turns the solution green, as does sodium sulfide.
Potassium ferricyanide changes the color to reddish-brown after two or three minutes. Depending upon the concentrations employed, the solution either remains clear or gradually deposits a brick-red flocculent precipitate.
Potassium chromate first turns the solution green and then gradually canary yellow.
A little zinc powder causes effervescence and eventually decolorizes the solution.

Titanium

- Titanium powder placed in a test tube containing hydrobromic acid appears not to react, even when heated. Very slowly, however, the reaction begins and a fine cloud of minute bubbles becomes visible. The liquid gradually acquires a lilac coloration. Several days are required before the reaction becomes clearly apparent. Once it has begun, however, very gentle warming is sufficient to accelerate it.

Tungsten

-A little tungsten powder is placed in a large, fairly tall test tube and covered with 33% hydrogen peroxide. At first, nothing appears to happen. Then small bubbles begin to rise from the surface of the powder. The reaction gradually accelerates and the tube becomes so hot that the process may eventually become quite vigorous. In the end, all the tungsten disappears and a colorless, strongly acidic liquid remains. This is pertungstic acid, formed by the action of hydrogen peroxide upon tungstic acid, H_2WO_4, which is yellow and insoluble and which itself forms slowly in less concentrated hydrogen peroxide.
Two reactions are therefore possible:
1) a relatively rapid reaction yielding colorless, soluble pertungstic acid;
2) a much slower reaction, sometimes requiring several weeks, yielding tungstic acid, which after evaporation and drying appears as yellow crystals.
It should be noted that if, in the first case, the test tube is cooled when the temperature is rising rapidly, the reaction becomes much less vigorous and remains permanently slowed thereafter.
Addition of baryta water produces a white curdy precipitate.
Ammonia gives a slight yellow coloration.
Potassium dichromate produces a black liquid accompanied by very vigorous foaming.

Mercury

- Mercury reacts with hydrogen peroxide. The reaction, which should be carried out in a test tube, begins slowly but after about ten minutes accelerates markedly and may even suddenly become explosive. Since a red-brown mercury oxide is formed, this experiment should be performed outdoors with the test tube placed well away from people and objects that might be struck by fragments or by the contents should the tube burst.

- Mercury is slightly attacked by a solution of hydriodic acid.

- Mercury is attacked at room temperature by sulfuric acid provided that a few drops of hydrogen peroxide are added. The reaction is not visible to the naked eye, however, because the salt formed is colorless. When heated with concentrated

sulfuric acid, mercury produces sulfur dioxide, as already described in the chapter devoted to the preparation of gases.

- Nitric acid attacks mercury at room temperature, but the products depend upon the concentration employed. Concentrated acid produces nitrogen dioxide directly, very dilute acid produces nitric oxide, and acid of intermediate concentration yields a mixture of nitric oxide and nitrogen dioxide corresponding to dinitrogen trioxide. As already noted, copper behaves in a similar manner.

IMPORTANT REMARKS CONCERNING MERCURY

Mercury, whether gathered into large droplets or dispersed into tiny ones, was long regarded as a kind of scientific curiosity and was sometimes even given to children as a plaything. In reality, it is a highly toxic substance whose vapors should not be inhaled. It is also a significant environmental pollutant.

When exposed to air, even while stored in its bottle, mercury gradually develops a superficial oxide film. For this reason, professional laboratories often purify mercury by distillation. In amateur or school laboratories, however, it is usually sufficient to wash the metal with water very slightly acidified with hydrochloric acid, shake the mixture in a separatory funnel, then decant and dry the mercury by rolling it in its bottle together with a small wad of filter paper.

Care should be taken to recover as much metallic mercury as possible after every experiment and to collect it in a dedicated container. These residues should periodically be cleaned as described above before being returned to the main stock.

- Two drops of mercury are placed in a test tube, after which an aqueous solution of iodine containing potassium iodide is added. The tube is set aside and the reaction allowed to proceed. It is extremely slow. At least twenty-four hours are required before decolorization of the iodine becomes noticeable near the surface of the mercury. If the tube is shaken only once or twice a day, the reaction may continue for several days. More vigorous and continuous agitation, however, greatly improves contact between the substances. Under these conditions, the iodine solution loses its color much more rapidly while the mercury becomes black and pasty.
If, on the other hand, mercury and iodine flakes are enclosed together in a stoppered test tube, colored patches slowly appear on the surface of the mercury. Two different iodides are thus formed.

- Mercury (100 parts), iodine (60 parts), and alcohol are triturated together for a prolonged period in a mortar. Green mercurous iodide is obtained. If this powder is heated in a test tube, it is transformed into red mercuric iodide and metallic mercury.

- Two or three drops of mercury are placed in a test tube and covered with bromine water. The contents are then agitated without heating. The bromine water gradually loses its color while a fine gray powder is deposited. The reaction proceeds more rapidly when the tube is shaken vigorously. In theory only one bromide should be formed, but in practice hydrolysis probably gives rise to two different bromides.

- The reactions of mercury with aluminum are particularly curious. The following examples illustrate some of them.
Take an aluminum plate approximately 2 mm thick and at least 3 × 4 cm in size. Using a drill fitted with an 8 mm metal bit, bore a shallow cavity into the plate, taking care not to drill all the way through. Clean the plate thoroughly and place one or two drops of mercury in the cavity. After more than fifteen minutes, nothing appears to happen. Remove the mercury and place a few drops of dilute hydrochloric acid in the cavity, allowing the liquid to extend slightly beyond its edge. Wait until small bubbles begin to appear over the entire surface of the metal beneath the acid, accompanied by a change in the appearance of the aluminum. Immediately blot the surface dry with absorbent paper and place the mercury back into the cavity. Within a few minutes, thin whitish-gray filaments begin to appear around the edge of the mercury. After one or two hours, a veritable hollow chimney composed of extremely fine, light-colored filaments may have formed, sometimes reaching a height of 8 to 10 cm (Figure 118). Eventually, this fragile structure collapses under its own weight or because of a slight air current. The material may be collected and dispersed in water, after which a variety of classical reagents may be tested upon it. Ammonia, for example, produces a precipitate of hydroxide, whereas sodium hydroxide solution produces none.

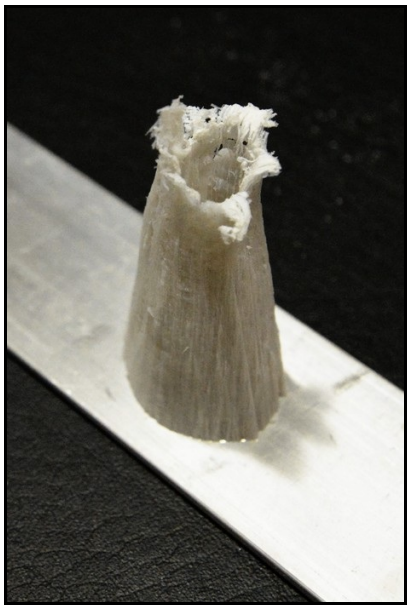


Figure 118

- The following is a variation of the preceding experiment. A little mercury, a ball of aluminum foil, and a few drops of water are enclosed in a stoppered test tube and maintained at gentle warmth for several days. A reaction gradually takes place. The aluminum becomes black and small white needles appear upon its surface.
Another variation may be performed as follows. An aluminum rod is first polished with emery paper and then immersed for one minute in a solution of mercury(II) chloride. It is removed and rinsed with distilled water. Holding the rod vertically, one presses it gently against filter paper in an attempt to remove as much water as possible without rubbing the surface. The rod is then suspended. Within minutes, white needles begin to grow and eventually fall as a powder onto the bench surface.

- A few drops of mercury brought into contact with a piece of sodium form a solid amalgam upon simple agitation. The reaction occurs suddenly, accompanied by a

flame and a little soot produced by ignition of the traces of petroleum that may still adhere to the sodium after its removal from the storage liquid. If this amalgam is immersed in water, hydrogen is evolved and, little by little, liquid mercury reappears while the colorless liquid becomes a solution of sodium hydroxide. If the amalgam is immersed in a fairly concentrated solution of ammonium chloride, it suddenly swells and develops blister-like protuberances resembling molten lava. This "lava" possesses the bright silvery appearance characteristic of pure mercury. In his well-known book *Récréations scientifiques*, Gaston Tissandier recommended carrying out this experiment in a narrow tube, from which the mercury would emerge as serpentine masses resembling metallic magma (Figure 119). In these two experiments, the mercury is completely recovered.

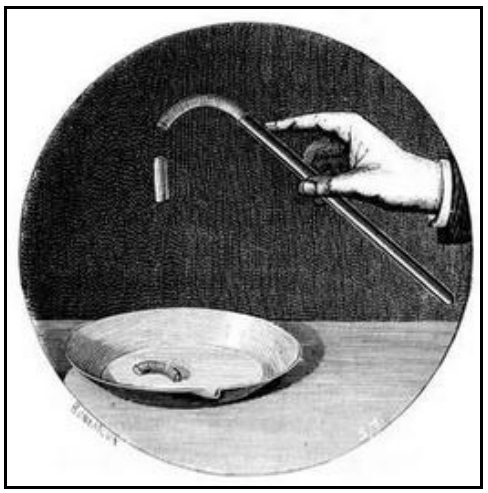


Figure 119

The amalgam may also be immersed in acetic acid. A vigorous reaction occurs and the mercury is once again recovered, while a solution of sodium acetate is formed.

- Mercury readily forms amalgams with silver and gold. The experiment may be performed using an old silver utensil or a small piece of gold leaf.
The fact that mercury emits vapor at ordinary temperatures may be demonstrated by suspending a piece of gold leaf above the mouth of a bottle containing mercury. The gold rapidly loses its luster and becomes gray.
Later in this book, we shall see how a gold object tarnished by mercury can be restored.

- Some chemists claim that prolonged grinding of magnesium powder with mercury in a mortar produces a magnesium amalgam. I attempted the experiment without success. Eventually, I placed the mixture in a test tube and agitated it for several minutes using a large IKA vortex mixer operating at maximum speed. No visible change occurred. Since the literature stated that this amalgam should react vigorously with water, evolving hydrogen and generating heat, I added water to the test tube. Hydrogen was indeed evolved, which might suggest that a small amount of amalgamation had occurred. However, magnesium powder placed in water at room temperature produces a rather similar effect. I therefore prefer not to draw any conclusion.

- Approximately 1 cm^3 of mercury and one or two zinc strips are placed in a large test tube. Water is then added, followed by sufficient hydrochloric acid to give a solution diluted by about one-third. A vigorous reaction immediately occurs but before long it slows and the bubbles are seen to originate only from the zinc, whose surface gradually becomes bright and shiny. Gentle warming is then applied. Fine bubbles now begin to emerge from the mercury as well. After a few minutes, the contents are agitated very vigorously, preferably with the aid of a mechanical

shaker. The zinc strip or strips become swollen while retaining their brilliant metallic appearance. The liquid is poured off, the amalgam is blotted dry, and the resulting zinc-mercury amalgam is stored in a tightly stoppered bottle.

- Copper powder is placed in a small beaker and covered with slightly acidified water in order to remove any oxide that may have formed on its surface. The beaker is placed on a magnetic stirrer and a few drops of mercury are added. Gradually, the appearance of the mixture changes and becomes darker. After a long time, stirring is stopped and the material is washed thoroughly with water. At the bottom of the vessel remains a bright metallic mass that is no longer nearly as mobile as ordinary mercury. This is a copper-mercury amalgam. When stored in a bottle, it eventually hardens completely, acquiring a gray color whose surface gradually develops a reddish tint. In this form it may be preserved indefinitely. When cut with wire cutters, the solid breaks with a characteristic creaking sound and crumbles. It is not attacked by water, even hot water, nor by hydrochloric acid. Immersed in concentrated nitric acid, however, it reacts vigorously, producing abundant red nitrous fumes and ultimately yielding a magnificent green solution.

- A test tube is charged with a 2 cm layer of mercury and then with a 1 cm layer of dilute sulfuric acid. A piece of copper foil is finally introduced. After a considerable time, an amalgam becomes visible upon the copper and the appearance of the metal changes. The copper may then be polished with a dry cloth to restore a brilliant surface.

- Potassium ferrocyanide initially appears to have no effect, but very slowly the liquid becomes cloudy and a precipitate forms. Depending upon concentration, this precipitate may remain white or may gradually color the liquid green and then blue, a process that may require as much as two days.

- A drop of mercury is placed in a test tube together with a few crystals of potassium permanganate, after which a little water is added. Mercurous oxide slowly forms and, if the mixture is boiled, is converted into mercuric oxide.

- A drop of mercury is placed in a test tube and covered with a concentrated potassium iodide solution. Basic potassium iodomercurate gradually forms.

- A silver nitrate solution is placed in a test tube and two drops of mercury are added. Only very slowly do small yellow needles begin to appear upon and around the surface of the metal.

- Sulfur flowers and mercury are ground together in a porcelain mortar. A black powder of mercury sulfide is obtained. This powder may then be strongly heated in a borosilicate 3.3 test tube. Sulfur vapors are evolved while a mercury mirror, or tiny droplets of mercury, form upon the walls of the tube. Under no circumstances should any mercury vapors produced during this operation be inhaled. In this way, cinnabar has been produced artificially and the industrial method formerly used to

obtain mercury has been recreated on a laboratory scale. Any mercury that failed to react in the mortar may be recovered by washing it with water containing a little hydrochloric acid.

- A Petri dish is placed on a perfectly level surface. A drop of mercury is introduced and allowed to spread into a flattened disk measuring roughly 1 cm^2. The mercury is then covered with well-diluted sulfuric acid. A few drops of potassium dichromate solution are added on the mercury, after which the drop is gently touched with the point of a large, sharp nail. The mercury immediately begins to move rhythmically, pulsing somewhat like a beating heart. In some cases, after the nail has been withdrawn, the pulsations continue for a time until the red precipitate becomes less abundant. To continue the experiment, it is sometimes necessary to remove part of this precipitate with a PVC pipette. This experiment has been known as the Beating Mercury Heart and also as the Mercurial Amoeba. It is described under that name in Wikipedia and related scientific literature. It does, however, require a certain degree of dexterity (See also page 69).

Silver

- Silver reacts at room temperature with hydrobromic acid and hydriodic acid, forming the corresponding salts and evolving hydrogen. It also reacts with nitric acid, producing silver nitrate and nitric oxide, which is immediately converted into nitrogen dioxide on contact with air.

- Silver immersed in an aqueous solution of hydrogen sulfide immediately becomes coated with a black layer of silver sulfide. The experiment may also be performed using gaseous hydrogen sulfide. Moisture promotes the reaction. Silverware must therefore be cleaned periodically because it reacts with the traces of hydrogen sulfide often present in the atmosphere, whether from cooking eggs or cabbage, sewer-gas emissions before changes in weather, the spreading of organic fertilizers, or similar sources.

Gold

- Two small beakers are filled respectively with concentrated hydrochloric acid and concentrated nitric acid. A small piece of gold leaf is placed in each beaker. Nothing happens. The contents of the two beakers are then poured into a third, larger vessel. The liquid gradually turns yellow, develops the odor of chlorine, and the gold leaf disappears rather rapidly. Aqua regia has thus been prepared, and the gold has been dissolved. Part of this liquid may be heated and concentrated by evaporation, then stored for subsequent experiments involving gold salts.

- A small, tightly stoppered 50 mL bottle is charged with 5 or 6 mL of ethyl alcohol. Three or four drops of bromine are added and the mixture is shaken to produce

bromo-alcohol. A small piece of gold leaf is then introduced and the bottle is stoppered. Before long, the gold leaf disappears completely. The liquid may subsequently be evaporated either in the open air or with gentle heating. A yellow-red gold salt is thus obtained.

Antimony

- Antimony is attacked by 68% nitric acid, although only slowly. A white powder is formed. Some authors state that this powder consists of antimony(III) oxide, which upon gentle calcination yields antimony oxide soluble in hydrochloric acid to produce antimony chloride.

A- ntimony is placed in sulfuric acid. At first, nothing appears to happen. After about twenty-four hours, however, the liquid acquires a distinctly pink coloration.

- Concentrated hydrochloric acid containing a little nitric acid reacts with antimony. Red nitrous fumes are evolved and, in principle, a solution of antimony trichloride ($SbCl_3$) together with residual substances remains.
The liquid may be concentrated to a syrupy consistency to obtain what was formerly called butter of antimony. Otherwise, the solution may simply be stored once the reaction has ceased. Addition of too much water would immediately decompose the salt.

- A little bromine is placed in a tall, wide test tube and antimony powder is added. The reaction is vigorous. After the bromine has evaporated, crystals of antimony bromide remain. Addition of water produces a white precipitate soluble in hydrochloric acid. If a bromine solution in carbon disulfide is used instead, the reaction is less vigorous than with bromine itself. After evaporation of the carbon disulfide, the same antimony bromide crystals are obtained.

- A bottle containing a solution of iodine in carbon disulfide is charged with a generous quantity of antimony powder and stoppered. The reaction may require several hours. The liquid gradually changes from brown-violet to yellow as antimony iodide forms. This iodide may be recovered by allowing the carbon disulfide to evaporate in sunlight.
If the iodine is dissolved in methyl alcohol instead, the reaction proceeds even more slowly and only gradually produces a deposit.

- A test tube containing a gold chloride solution receives an antimony crystal about the size of a pea. The crystal soon becomes coated with a red film consisting of a thin layer of gold, while the solution gradually loses its color. Subsequently, if the gold chloride solution was acidic, the antimony is attacked and a white muddy material is formed.

Arsenic

- A few drops of bromine poured onto arsenic produce a very vigorous reaction. Great caution is necessary.

Phosphorus

- A small stemmed glass of approximately 150 mL capacity is charged with zinc powder and very small zinc granules. A layer of water about 2 cm deep is added, followed by fairly small pieces of yellow phosphorus. The apparatus is placed outdoors in a well-ventilated location. A few drops of concentrated hydrochloric acid are then added and the operator immediately moves away. Hydrogen begins to evolve and is gradually replaced by a white smoke accompanied by a garlic-like odor. Small sparks may even be observed at the surface of the liquid. Nascent hydrogen combines with phosphorus to form impure phosphine, which ignites spontaneously in air. A thin layer of sawdust floating on the surface sometimes makes the ignitions easier to observe.

- Yellow phosphorus is dissolved in carbon disulfide and iodine is gradually added with agitation after each addition. Each addition initially produces a brown coloration which, after sufficient agitation, changes to yellow-orange. If the experiment is stopped at this stage and the mixture is allowed to stand, the yellow phosphorus is converted into red phosphorus, which precipitates. If, however, iodine continues to be added until the liquid retains a distinctly red color and the mixture is then cooled below 0 °C, red crystals of phosphorus iodide are deposited.

- A piece of yellow phosphorus is dissolved in carbon disulfide. A few drops of this solution are placed upon filter paper and allowed to evaporate. As soon as evaporation is complete, the filter paper ignites.

- A piece of yellow phosphorus enclosed in a small bottle containing concentrated ammonia gradually becomes black. This is a long-term experiment requiring considerable patience.

- A piece of phosphorus is enclosed in a copper sulfate solution. Gradually, the phosphorus becomes coated with a black layer of copper phosphide while the liquid loses its blue color.

Selenium

- A little selenium and slightly diluted nitric acid are placed in a test tube or small Erlenmeyer flask. The mixture is warmed very gently to initiate the reaction, which produces abundant red-brown fumes. If necessary, additional selenium may be added until no further attack occurs. The liquid remains green because dissolved gas

is still present. It is then transferred to a wide-necked bottle and shaken until it becomes colorless. This liquid contains selenium dioxide, SeO_2, which reacts with the water present in the acid to form selenious acid, H_2SeO_3. The preparation of selenious acid has already been described on page 119. A quantity of sodium sulfite crystals about the size of a pea is then added to this acid. The liquid gradually develops a beautiful orange coloration, then turns brick red, and finally deposits red selenium. The same phenomenon occurs if a piece of zinc is placed in the solution. If the solution still contains excess acid, the zinc first evolves gas for a time before the red selenium begins to appear.

- A layer of nitric acid three or four centimeters deep is poured over selenium powder in a test tube. Before long, the liquid becomes yellow and a white powder of selenium dioxide, SeO_2, becomes visible.
If, on the other hand, nitric acid is allowed to act upon a lump of selenium, attack occurs only after slight warming and is accompanied by the evolution of abundant red nitrous fumes.

12.2 Reactions Involving Halogens and Halides

Chlorine

- An aqueous solution of iron(II) sulfate is poured into two beakers. Chlorine water is added to the first beaker. The color changes from pale green to very light yellow. A solution of sodium or potassium hydroxide is added to the second beaker. A pale greenish-white precipitate is formed. Chlorine water is then poured onto this precipitate and the mixture is stirred. The precipitate becomes brick red. Finally, sodium or potassium hydroxide solution is added to the contents of the first beaker. An identical brick-red precipitate immediately appears.

- A little chlorine water is added to a solution of potassium or sodium iodide. Depending upon the concentration of the iodide solution, the liquid becomes brown or almost black, while small flakes possessing metallic reflections are liberated. The addition of a little chloroform readily demonstrates the liberation of iodine, since after agitation part of the liquid assumes a violet-purple coloration.

- A little chlorine water is added to a solution of sodium or potassium sulfide. A colloidal precipitate of sulfur is formed.

Bromine

- Bromine water is added gradually to a freshly prepared solution of sulfurous acid. The bromine color disappears progressively. The resulting liquid is tested with an aqueous solution of barium chloride. A white precipitate appears, indicating the

formation of a mixture of sulfuric acid and hydrobromic acid.

- Bromine is added dropwise to a concentrated potassium hydroxide solution placed on a magnetic stirrer. Each drop initially becomes decolorized. Little by little, white crystals of potassium bromate appear while the liquid acquires a reddish color owing to the dissolution of part of the bromine. When bromine is no longer consumed, the mixture is filtered. The insoluble bromate remains on the filter. The filtrate is heated. Bromine escapes rapidly and the liquid becomes colorless. It contains dissolved potassium bromide. A portion of this solution is evaporated rapidly with a hair dryer or an infrared heater. Manganese dioxide and sulfuric acid are then added and the mixture is warmed gently. Bromine is liberated.

- Bromine or bromine water is added gradually to dilute ammonia. Especially when pure bromine is used, nitrogen is evolved. Ammonium bromide is formed. The liquid is concentrated by heating in a test tube until white crystals of ammonium bromide become visible. A pinch of manganese dioxide and a few drops of concentrated sulfuric acid are then added and the mixture is heated. Bromine is evolved.

- The reaction between sodium thiosulfate and iodine is well known and yields a completely colorless liquid. For this reason, sodium thiosulfate was formerly used to remove iodine stains. Bromine behaves somewhat similarly, except that in this case a milky sulfur precipitate is formed.

- A little cyclohexane is added to bromine water and the mixture is shaken. The bromine passes into the cyclohexane layer. Nothing similar occurs with benzene.

- A little bromine water is added to a solution of potassium or sodium iodide. Depending upon the concentration of the iodide solution, the liquid becomes light brown or nearly black while metallic-looking flakes of iodine are liberated. The addition of a little chloroform readily demonstrates the liberation of iodine.

- A little bromine water is added to an iron(II) sulfate solution. An immediate color change occurs. Addition of sodium hydroxide confirms that the solution now yields a reddish-brown precipitate of iron(III) hydroxide, showing that the ferrous salt has been converted into a ferric salt.

- Liquid bromine is placed in a wide test tube and sulfur is added little by little. The temperature rises and sulfur monobromide, S_2Br_2, is formed. If water is added, slow hydrolysis occurs. Sulfur is deposited while hydrobromic acid and sulfur dioxide are liberated. The hydrolysis is accelerated by the addition of a little sodium bicarbonate or potassium hydroxide to the water. The experiment may also be carried out in reverse.

- Sulfur bromide is first prepared by adding sulfur flowers to bromine with agitation. The liquid gradually becomes more orange and increasingly viscous. A few drops of concentrated ammonia are then added, the sulfur bromide being diluted beforehand

with carbon disulfide if necessary. A color change is observed and, after some time, the mixture solidifies. This experiment cannot be performed in a classroom because of the extremely unpleasant odor of both sulfur bromide and carbon disulfide. Furthermore, the reaction is rather unpredictable, the results seeming to depend greatly upon the quantities employed. According to some chemists, the final products should be ammonium bromide and nitrogen, accompanied by considerable heat evolution. Some even claim that the mixture may ignite if a little phosphorus is added to the carbon disulfide. Frankly, I have not observed these phenomena.

- A little sulfur flowers are placed in a small bottle that can easily be closed, and bromine is then added. The bottle is stoppered and shaken. An oily liquid is obtained whose odor recalls that of sulfur chloride. When poured into water, it forms small red globules.

- Bromine dissolved in carbon disulfide is prepared in one bottle, while yellow phosphorus dissolved in carbon disulfide is prepared in another. The two solutions are then mixed gradually. The yellow color intensifies while the bromine color disappears. The mixture is exposed to sunlight and allowed to evaporate. Phosphorus bromide is obtained.

- Bromine water is added to an aqueous solution of sodium sulfite. The bromine is decolorized and the liquid becomes acidic owing to the formation of hydrobromic acid.

- Two or three drops of bromine react with a few drops of ether or a few drops of methyl alcohol placed in a test tube. In both cases, the reaction remains moderate.

- A drop of bromine is added to an acetic solution of fluorescein. Eosin is formed.

- A mixture is prepared by adding a few drops of aniline to water and making the solution slightly alkaline. Bromine water is then added. A reddish-brown precipitate is obtained. Conversely, if the water-aniline mixture is made slightly acidic before the bromine water is added, a pale yellowish-white precipitate of tribromoaniline is formed.

- Solid sodium citrate is dissolved in bromine water with agitation. The mixture is gently heated. The liquid becomes colorless, carbon dioxide is evolved, and bromoform together with another compound known as bromoxaform is produced. The characteristic odor of bromoform is readily detected.

- Bromine water, or even bromine itself, is added gradually to a concentrated aqueous solution of phenol. A white flocculent precipitate of tribromophenol is formed. This precipitate dissolves in alcohol.

- If a few drops of bromine are allowed to fall directly onto phenol crystals, the reaction is extremely vigorous. Caution is therefore required.

- Bromine water is added to a solution of salicylic acid. A yellow precipitate first appears, followed by a white precipitate of tribromophenol derivative.

Iodine

- The reaction between iodine and starch is well known. If the starch is dry, a brown coloration is obtained. If a starch solution is used, a blue coloration appears. When the blue solution is heated, the color disappears and reappears upon cooling. If heating has been prolonged excessively, however, the blue coloration no longer returns.
It has also been observed that, in a blue starch solution containing only a moderate quantity of iodine, the addition of alcohol changes the color successively to violet, red, and sometimes even yellow.
A less familiar observation is that bromine produces an intense yellow coloration when substituted for iodine.

- A solution of iodine in water or ethyl alcohol is decolorized at room temperature by a solution of ascorbic acid.

- Iodine flakes are dissolved little by little in a concentrated potassium hydroxide solution placed on a magnetic stirrer. The liquid becomes yellow and a white precipitate of potassium iodate gradually appears. The colored liquid contains potassium iodide. If the insoluble iodate were calcined, it too would eventually be converted into potassium iodide.

- A solution of phosphorus in carbon disulfide is mixed with a solution of iodine in carbon disulfide. Decolorization occurs owing to the formation of phosphorus iodide.

- Five or six cubic centimeters of carbon tetrachloride are placed in a test tube and a few drops of iodine tincture are added. The initially brown liquid assumes a beautiful coloration ranging from pink to yellow.

- An iodine solution in ethyl alcohol is prepared. A second alcoholic solution containing potassium hydroxide is prepared separately. With vigorous agitation, the alkaline solution is added slowly to the iodine solution until the brown color disappears. The liquid is then allowed to cool. Beautiful silky yellow crystals of iodoform are deposited. Iodoform was once widely used as an antiseptic, and its characteristic odor was familiar in the medical offices of an earlier era.

- A few drops of alcoholic iodine solution added to an aqueous solution of potassium ferrocyanide produce a yellow precipitate. In an aqueous solution of potassium ferricyanide, a brick-red precipitate is obtained instead.

- The following series of curious and rather complex reactions is described by J. W.

Mellor in *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (London, 1922, Vol. 2, pp. 247–248).
A little aqueous iodine solution is placed in a 100 mL Erlenmeyer flask. A small quantity of potassium iodide may be added beforehand to facilitate dissolution of the iodine. Potassium hydroxide solution is then added dropwise until the color becomes golden yellow. A portion of this liquid is subsequently added to ink-colored water, hydrogen peroxide, a cobalt salt solution, a manganese salt solution, and a lead salt solution.
The ink is decolorized.
Oxygen is rapidly evolved from the hydrogen peroxide, and the reaction gradually accelerates while generating considerable heat.
A black precipitate appears in the cobalt solution, whereas a brown precipitate is obtained in the manganese and lead solutions. These reactions resemble those produced by potassium or sodium hypochlorite and hypobromite.
The original yellow solution is the site of a complex reaction and gradually loses both its color and its decolorizing properties.
If the golden-yellow solution is first brought to a boil before the experiments are carried out, a blue-green precipitate appears in the cobalt solution, a yellow-brown precipitate in the manganese solution, and a lemon-yellow precipitate in the lead solution. These changes result from a profound modification in the composition of the solution.

- An iodine solution is prepared in water containing sodium or potassium iodide. A fragment of calcium carbide is introduced and the mixture is shaken. The reaction is immediate and produces a considerable quantity of gas together with a peculiar odor that differs from that of acetylene. The liquid changes from brown to yellow and eventually becomes colorless. Iodoform and diiodoform appear to be formed. The liquid should be decanted immediately to avoid contamination by the usual white residue produced when the carbide decomposes completely. One or two drops of concentrated sulfuric acid are then added. The iodine color reappears.

- A little iodine is placed in a small porcelain dish. A few drops of turpentine are then allowed to fall onto it. A small cloud of iodine vapor immediately appears. If more turpentine is added until the iodine crystals are completely submerged, the dish gradually fills with a black, greasy mass.

- A little iodine is placed in a small crucible and a few drops of lavender oil are allowed to fall onto it. A slight detonation occurs with each addition and yellowish-brown vapors are evolved. An oily substance having the color of iodine remains behind.

Hydrobromic and Hydroiodic Acids

- Chlorine water added to a hydrobromic acid solution liberates bromine, which may readily be extracted into chloroform or carbon disulfide.

- When hydrobromic acid is poured onto manganese dioxide, an orange-red coloration appears, indicating the liberation of bromine. Gentle heating produces a clearly visible quantity of bromine vapor in the upper part of the test tube.

- If hydrobromic acid is poured onto lead dioxide, the black solid appears to disappear, yielding an orange-colored liquid.

- Addition of a few drops of silver nitrate to hydrobromic acid produces a white precipitate which immediately disappears. More silver nitrate must be added before the pale yellowish-white precipitate becomes permanent.

- A little hydrobromic acid is placed in a test tube and a very small quantity of potassium permanganate is added. Instead of becoming violet, the liquid turns greenish-yellow and then canary yellow. Additional permanganate intensifies the yellow coloration. Gentle warming causes red bromine vapor to appear in the upper part of the test tube.

- Concentrated nitric acid is added gradually to a hydrobromic acid solution. The initially colorless liquid becomes progressively red, warms spontaneously, and eventually releases bromine, recognizable by both its color and odor. This mixture constitutes a kind of aqua regia capable of dissolving gold. If acids that are not sufficiently concentrated are used, especially in the case of nitric acid, nothing appears to happen. The liquid should then be heated gently, concentrating the flame chiefly near the upper portion of the solution. As soon as a brownish-red coloration appears, heating is stopped. The color then spreads progressively through the liquid while bromine vapor begins to accumulate above it (Figure 120).
A similar experiment may be carried out using hydriodic acid in place of hydrobromic acid.

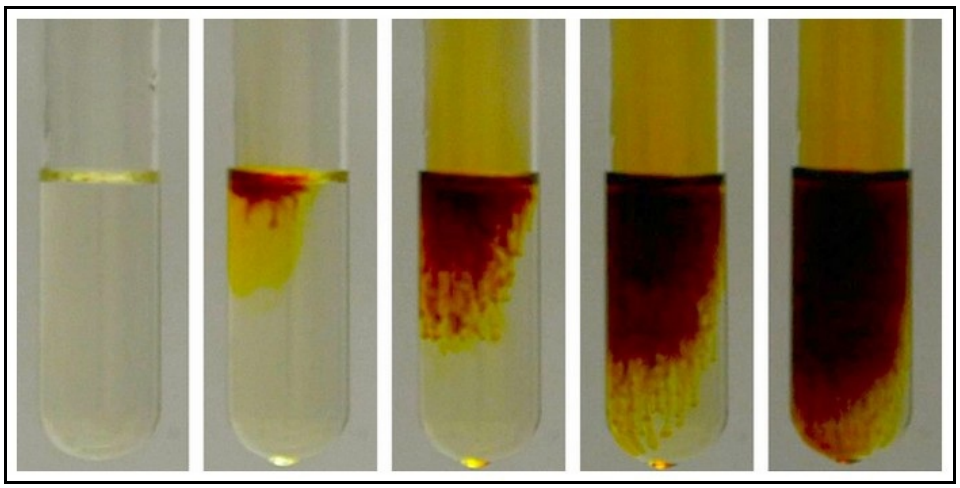


Figure 120

- Chlorine water or sodium hypochlorite solution (bleach) added to hydriodic acid liberates iodine.

- Bromine water added to hydriodic acid likewise liberates iodine, which may readily be identified by extraction into chloroform.

- A little freshly prepared sulfurous acid added to hydriodic acid colors the liquid yellow owing to the liberation of a small quantity of dissolved iodine.

- A hydriodic acid solution containing a trace of hydrochloric acid turns brown immediately when hydrogen peroxide is added, owing to the liberation of iodine.

- Fragments of antimony, iron, tin, zinc, copper, magnesium, manganese, together with a few drops of mercury, are placed in separate test tubes and covered with hydriodic acid. After waiting for some time, it is found that only iron, zinc, manganese, and magnesium react to any noticeable extent, even upon warming. This demonstrates that, despite its low pH, hydriodic acid remains a relatively unreactive acid within its own family.

- Several cubic centimeters of hydriodic acid are placed in four separate test tubes. A few drops of sulfuric acid are added to the first, a substantial quantity of sulfurous acid to the second, and a few drops of nitric acid to the third. In the first case, the greater density of the sulfuric acid causes a brown coloration to spread through the bottom of the tube. In the second case, the liquid becomes uniformly yellow. In the third, a brown coloration gradually spreads throughout the solution. In each of these three cases, iodine has been liberated, although to varying degrees. Hydrochloric acid is added to the fourth test tube. Nothing appears to happen. After about ten hours, however, even this tube has acquired a pale yellow coloration. In the tube containing nitric acid, a layer of small iodine crystals may be observed at the bottom.

- A precipitate of silver chloride is prepared by mixing silver nitrate and sodium chloride solutions. Hydriodic acid is added immediately. The white precipitate becomes yellow owing to the formation of silver iodide.

- A white precipitate of lead chloride is prepared by mixing lead acetate and sodium chloride solutions. Hydriodic acid is then added. The precipitate immediately assumes a beautiful canary-yellow color owing to the formation of lead iodide.

- Mixing a solution of mercury(II) chloride with hydriodic acid produces a magnificent orange precipitate of mercury iodide.

Bromides, Iodides, and Iodates

- Chlorine water added to a bromide solution liberates bromine.

- A potassium bromide solution is poured into bleach. Vigorous foaming occurs, the liquid becomes warm, and bromine is liberated. The same experiment may be performed with potassium iodide solution, in which case iodine is liberated.

- A little crystalline potassium bromide is placed in a small bottle and concentrated sulfuric acid is added. A colorless foam immediately appears. If the evolved gas is collected in a little water and chlorine water is then added, the solution immediately turns orange-red, showing that hydrobromic acid had dissolved in the water. This acid also fumes strongly in moist air if allowed to escape freely. An aerosol spray may be used to demonstrate this effect. After a short time, however, the highly exothermic reaction changes character and bromine vapor begins to appear in the bottle. Soon, the crystals and the foam become orange-red, indicating a substantial evolution of bromine. Consequently, this reaction is not really suitable for the convenient preparation of hydrobromic acid solutions, except perhaps when only a very small quantity is required urgently.
If potassium iodide is used instead of potassium bromide, iodine is liberated immediately and rapidly coats the walls of the bottle. This reaction is therefore entirely unsuitable for preparing hydriodic acid solutions, even in an emergency.

- Four small beakers are prepared containing equal quantities of potassium bromide solution, and four additional beakers containing equal quantities of potassium iodide solution. Three gaseous solutions are prepared separately: chlorine, hydrogen sulfide, and sulfur dioxide. Bromine water is also prepared. Each of these four reagents is then added to one of the potassium bromide solutions and to one of the potassium iodide solutions. Depending upon the case, bromine or iodine is liberated. Iodine may readily be identified and extracted with chloroform, which acquires a violet coloration. Alternatively, starch paste may be added, producing a violet-colored suspension.
The same experiments may be carried out by bubbling chlorine, hydrogen sulfide, or sulfur dioxide directly through solutions of potassium bromide or potassium iodide.

- A quantity x of potassium iodide is dissolved in water and the solution is divided equally between two small beakers. An equal weight x of mercury(II) chloride is dissolved in the same volume of water and this solution is likewise divided equally between two additional beakers. Four beakers are therefore available: two containing potassium iodide solution and two containing mercury(II) chloride solution.
(a) One potassium iodide solution is added slowly to one of the mercury(II) chloride solutions. Red mercury iodide is formed.
(b) Conversely, one mercury(II) chloride solution is added gradually to the remaining potassium iodide solution. An orange-pink precipitate of potassium tetraiodomercurate, K_2HgI_4, appears but dissolves immediately.
Thus, depending upon which reagent is initially present in excess, the course of the reaction differs markedly.
If the liquid above the red precipitate is evaporated completely and heating is continued briefly, the precipitate becomes yellow. If a sodium thiosulfate solution is added instead, the precipitate disappears completely.

- A few crystals of potassium iodide are added to nitric acid. The liquid becomes

brown and nitrogen dioxide is evolved. Water, potassium nitrate, and iodine are also formed. The iodine may readily be demonstrated by extraction with chloroform, which acquires a violet coloration upon agitation.

- A strongly acidified ferric chloride solution is prepared by adding hydrochloric acid. A potassium iodide solution is then added. The liquid immediately becomes brown owing to the liberation of iodine. Addition of chloroform and agitation readily confirm its presence.

- A milk of lime is prepared and an iodine solution containing a little potassium iodide is added gradually until the liquid acquires a yellowish tint. The resulting liquid may be regarded as a form of bleaching powder analogue containing iodine. When added to an alkaline magnesium salt solution, it produces a brown precipitate that gradually settles. Addition of sodium thiosulfate causes the precipitate to disappear immediately.
Alternatively, the mixture may be shaken with chloroform, which becomes colored and thereby demonstrates the presence of iodine.

- Hydrogen peroxide added to an alkaline iodide solution liberates iodine and causes a vigorous evolution of oxygen.
A particularly striking variation consists of mixing a few potassium iodide crystals with a small quantity of dishwashing liquid and then pouring hydrogen peroxide directly over the mixture. A large volume of colored foam rapidly overflows from the vessel, clearly demonstrating the abundant gas evolution. This experiment, extremely popular on the internet and especially on YouTube, has become known as Elephant Toothpaste. It was already mentioned earlier in this book.

- The following substances are mixed in succession: a little potassium iodide solution, a few drops of dilute sodium hydroxide solution, and finally a little mercury(II) chloride solution. A red precipitate of mercury iodide is formed. Addition of a little dilute ammonium hydroxide causes the precipitate to become even more pronounced.

- A sodium nitrite solution is prepared and two drops of hydrochloric acid are added. A reddish gas is evolved, but this may be disregarded. Potassium iodide solution is then added. The liquid immediately becomes brown owing to the liberation of iodine, which may be demonstrated with either chloroform or starch paste.

- A little acetic acid is added to an ammonium nitrate solution, followed by potassium iodide solution. A faint yellow coloration may appear owing to the liberation of a small quantity of iodine. Zinc powder is then added. The color deepens to dark yellow or even brown. Finally, a little carbon disulfide is added and the mixture is shaken. A violet drop of iodine solution appears.

- To 250 mL of water are added 25 g of potassium iodide, 1 g of potassium hydroxide, and 3 g of aceton. After vigorous agitation, dilute sodium hypochlorite

solution is added until no further yellow precipitate appears where the liquids come into contact. The characteristic odor indicates the formation of iodoform.

- Three test tubes are charged with potassium iodide solution containing a few drops of starch solution. Chlorine water is added to the first, nitric acid to the second, and sulfurous acid to the third. The first two tubes immediately develop a violet coloration, indicating the liberation of iodine. The third becomes only slightly yellow as sulfurous acid is added.
A similar experiment may be performed with potassium iodate solution in place of potassium iodide solution. Again, chlorine water is added to the first tube, nitric acid to the second, and sulfurous acid to the third. Nothing occurs in the first two tubes. The third, however, immediately turns blue, demonstrating the liberation of iodine.

12.3 Reactions Involving Mineral Salts

Calcium, Sodium, Potassium, and Ammonium Salts

- Excess powdered calcium hydroxide is added to a moderately concentrated sodium carbonate solution. The mixture is stirred and filtered. The white solid now consists chiefly of calcium carbonate, the principal constituent of marble, while the filtrate contains sodium hydroxide (caustic soda).

- Hydrogen peroxide is added gradually to limewater. A white precipitate of calcium peroxide is formed. A few drops of hydrochloric acid are sufficient to dissolve it.

- Two solutions are prepared, one containing ammonium oxalate (or oxalic acid) and the other a soluble calcium salt such as calcium chloride. Upon mixing, a white precipitate is formed. This precipitate disappears upon addition of nitric acid. In very dilute solutions, precipitation occurs only slowly. A drop of ammonia may facilitate its formation.

- A saturated calcium chloride solution is prepared and poured into a beaker or crystallizing dish. Dilute sulfuric acid is then added until no further precipitate forms. The mixture is stirred thoroughly and allowed to settle. The excess liquid is decanted and the precipitate is dried in a silicone mold. When completely dry, it is crushed in a mortar and heated to a temperature not exceeding 120 °C. It is then mixed with a little water and returned to a mold. Plaster of Paris has thus been prepared and sets rather rapidly.

- A test tube is charged with a saturated sodium hydroxide solution that has been standing long enough to return to room temperature. Hydrogen peroxide is carefully layered on top. An abundant white foamy precipitate immediately fills the tube. If a less concentrated sodium hydroxide solution is used, nothing appears to happen. In that case, the addition of absolute alcohol causes a mucilaginous, foamy precipitate to appear. This precipitate disappears when sufficient water is added.

It consists of sodium peroxide.

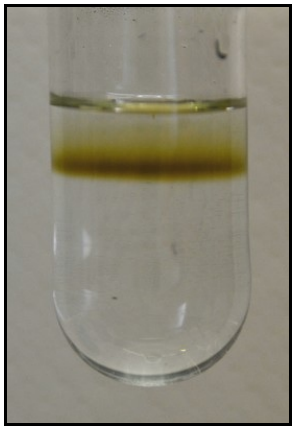


Figure 121

- Three or four centimeters of sodium nitrite solution are placed in a test tube and approximately half that volume of sulfuric acid is added. After mixing, the tube is placed for a few minutes in an ice bath. A solution of ammonium iron(II) sulfate is then allowed to flow slowly down the wall of the tube in order to prevent rapid mixing. At the interface between the two liquids, a greenish-brown ring gradually appears, depending upon the concentrations employed. This complex is known as the Richmond Ring (Figure 121). The acidic medium accelerates its formation.

- A mixture of chromic acid and hydrochloric acid is prepared. This mixture is added dropwise to a sodium nitrite solution that is being stirred mechanically or magnetically (Figure 122). The liquid gradually changes color owing to the formation of chromium chloride, becoming green or even blue-violet when the original chromic acid solution was highly concentrated. Throughout the experiment, nitrogen dioxide is evolved. By the end, the liquid may even foam. The experiment should therefore be carried out in a well-ventilated room.

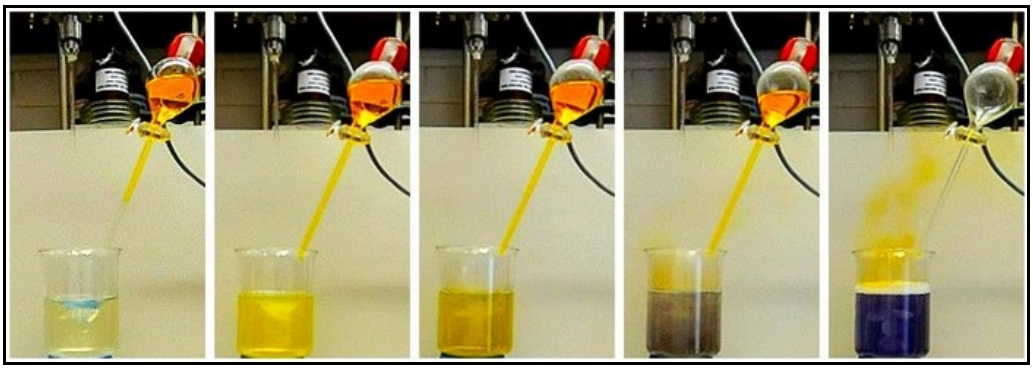


Figure 122

- A hydrochloric acid solution diluted to about half its usual concentration and a fairly concentrated sodium nitrite solution are prepared separately. They are then placed in a freezer for a short time until their temperature falls to about 8 °C. The two solutions are subsequently mixed in a vessel surrounded by an ice-water bath. A blue solution of nitrous acid is obtained. The experiment must be carried out below 10 °C, otherwise the nitrous acid decomposes rapidly. Hydrochloric acid may be replaced by sulfuric acid with the same result.
The nitrous acid thus prepared liberates iodine from iodide solutions, decolorizes an acidified permanganate solution, and forms a red dye when poured into aniline or onto solid phenol. The latter two test tubes should subsequently be rinsed with aceton.
When exposed to sunlight or heated, nitrous acid liberates red nitrous fumes and gradually loses its color. Heating accelerates the process still further. Vigorous

agitation produces abundant foaming, sometimes sufficient to cause the liquid to overflow. Caution is therefore required. Several properties of this unstable acid were already described on pages 196-197.

- A sodium nitrite solution is added to an aqueous copper sulfate solution. The original blue liquid acquires a beautiful emerald-green coloration.

- Sodium nitrite solution is poured into a test tube and a little sodium sulfide solution is layered above it. Nothing happens. One or two drops of hydrochloric acid are then added. A yellow sulfur precipitate immediately appears. The acid should not be added before the sulfide solution, since it would react directly with the nitrite.

- Sodium nitrite solution is placed in a test tube and a little potassium iodide solution is layered above it. Again, nothing happens. A little acetic acid is then added. The liquid turns brown. Chloroform is added and the mixture is shaken. The chloroform extracts the brown coloration, showing that iodine has been liberated

- Three stemmed glasses or three beakers are prepared, each containing the same sodium thiosulfate solution. Dilute hydrochloric acid is added to the first vessel, moderately concentrated hydrochloric acid to the second, and concentrated hydrochloric acid to the third. Instantly, or after a few seconds, a sulfur precipitate appears. After allowing the mixtures to stand, it is observed that the amount of sulfur formed increases with the concentration of the hydrochloric acid.

-A sodium thiosulfate solution is placed in an Erlenmeyer flask and concentrated nitric acid is added. Within a very short time, the liquid becomes yellow owing to the deposition of sulfur and the flask fills with red fumes.

- A sodium thiosulfate (hyposulfite) solution poured into selenious acid produces a brick-red to reddish-brown precipitate. It appears slowly or rapidly, in small or large amounts, depending on the concentrations and on whether the solution is heated.

- If nitric acid is poured directly onto solid sodium thiosulfate, the reaction becomes almost instantaneous. A large volume of red fumes is released into the atmosphere while fragments of solid sulfur remain in the flask. After a rapid washing with water, these sulfur fragments may even be compressed between the fingers.

- Four centimeters of sodium thiosulfate solution are placed in each of five test tubes. The first tube is set aside as a reference. A little chlorine water is added to the second, bromine water to the third, sodium hypochlorite solution (bleach) to the fourth, and freshly prepared sodium hypobromite solution to the fifth. Depending upon the concentrations employed, a white cloudiness or a white precipitate appears in test tubes 2 and 3. They are warmed gently to remove any excess chlorine or bromine. The contents of test tubes 4 and 5 appear unchanged. A few drops from each of test tubes 1 through 5 are then transferred respectively into test

tubes 6 through 10, each containing about 3 cm of barium chloride solution. A white precipitate forms in every tube except number 6, which received the untreated thiosulfate solution. Careful observation is required for test tubes 7 and 8 because their contents were already cloudy before the addition of barium chloride. Nevertheless, additional cloudiness is clearly produced. The conclusion is that the thiosulfate ion, which does not react with barium chloride, has been transformed in test tubes 2 through 5 into sulfate ions, which do yield a white precipitate with barium chloride.

- Sodium metabisulfite (also known as sodium pyrosulfite) mixed with water releases sulfur dioxide. If powdered magnesium or small magnesium turnings are then added, magnesium sulfite, sodium sulfite, and—rather unexpectedly—hydrogen gas are produced.

- A sodium oxalate solution is treated with barium chloride solution. A heavy white precipitate is formed. This precipitate disappears rapidly upon addition of hydrochloric acid and much less readily upon addition of oxalic acid solution.

- A little solid sodium bicarbonate is mixed with solid citric acid in a test tube and moistened with water. Vigorous effervescence occurs. Effervescent tablets operate according to this same principle.

- A potassium hydrogen sulfate solution is prepared and treated with a solution of sodium carbonate or sodium bicarbonate. Vigorous effervescence occurs owing to the evolution of carbon dioxide.
The same experiment may be performed differently. The two dry salts are simply mixed in a test tube and a little water is added from a wash bottle. Immediate and vigorous effervescence follows.

- Dilute hydrochloric acid is poured onto potassium chlorate. If no reaction is observed, concentrated hydrochloric acid is added until gas evolution begins. The test tube is allowed to fill with the evolved gas. Examination shows that chlorine is being produced.

- Place about 1 cm^3 of potassium chlorate in a stemmed glass standing in a crystallizing dish, then pour 10–15 mL of sodium bisulfite solution over it. Small bubbles slowly begin to form and rise to the surface while the liquid turns yellow. Chloric acid is in fact being produced. After a short time, however, the reaction suddenly accelerates and the liquid foams up vigorously. The odor of sulfur dioxide then becomes noticeable. Perform this experiment outdoors.

- An alkaline sulfide solution is added to a potassium hydrogen sulfate solution. A sulfur precipitate forms immediately and a slight effervescence is observed. Gentle warming subsequently reveals the characteristic unpleasant odor of hydrogen sulfide.

- In a first beaker, dilute sulfuric acid is poured onto a small quantity of zinc. Hydrogen begins to evolve. Separately, an aqueous solution of potassium chlorate or sodium chlorate is prepared. A portion of this solution is tested with silver nitrate and found not to produce any precipitate, demonstrating the absence of chloride ions. The chlorate solution is then added to the beaker in which nascent hydrogen is being generated. After some time, a sample of the liquid is transferred to a test tube and tested again with silver nitrate. A precipitate now appears. Nascent hydrogen has reduced the chlorate ion to chloride.

- Hydrogen peroxide is added to an alkaline potassium ferricyanide solution. Oxygen is evolved.

- A potassium ferrocyanide solution is boiled in order to expel dissolved air. If the liquid does not completely fill the bottle, the remaining space is filled with carbon dioxide and the bottle is closed tightly. After cooling, a large flask is prepared containing sufficient hydrochloric acid to provide an excess relative to the ferrocyanide. A layer of ether is carefully added above the acid, after which the ferrocyanide solution is introduced. The mixture is shaken. A large bluish-white precipitate of ferrohydrocyanic acid is formed. Its appearance varies according to concentration. In some cases, when dispersed throughout the liquid, it may even appear slightly greenish. Dilution with water causes the precipitate to collect near the top of the vessel.
Another version of the same experiment may be performed. A tall beaker is filled with a distinctly yellow potassium ferrocyanide solution. A layer of ether corresponding to roughly one-fifth of the volume of the solution is poured on top. The vessel is covered with a cardboard sheet or glass plate provided with a central opening. The contents are then agitated vigorously using a suitable mixer. The Vibromix stirrer (Figure 24) is particularly well suited to this operation. A concentrated hydrochloric acid solution is then poured onto the emulsion. An immediate bluish-white, highly granular precipitate of ferrohydrocyanic acid appears. The excess liquid is poured away and the precipitate is dried either in sunlight or with a hair dryer. It rapidly acquires the characteristic color of Prussian Blue. Water may also be added to the vessel and the mixture agitated. A beautiful emerald-green liquid then appears, surmounted by a smaller quantity of the original white precipitate. This liquid likewise turns blue gradually on exposure to air.

- A concentrated potassium hydroxide solution is prepared in isopropyl alcohol. Carbon disulfide is then added. A yellow mass forms immediately and the temperature rises slightly. One particularly interesting observation is that the repulsive odor of carbon disulfide is replaced by a much milder and somewhat sweet odor. A potassium thiocarbonate has been formed.

- Five milliliters of aniline are mixed with a cooled solution prepared from 5 mL of sulfuric acid diluted in 100 mL of water. A further 100 mL of concentrated sulfuric acid are then added. This mixture is poured into a potassium chlorate solution. Several color changes occur. The operation should be carried out cautiously and

with thorough agitation, since excessive concentrations of potassium chlorate may create a hazardous situation.
For this reason, only a relatively dilute chlorate solution should be employed. The succession of colors obtained during the reaction is particularly striking.

Iron Salts (II) and (III)

- A potassium ferrocyanide solution is added to an iron(II) sulfate solution. A beautiful ink-blue coloration is obtained. Ammonia is then added and the blue color disappears. Addition of hydrochloric acid restores it.

- A solution of sodium phosphate is treated slowly with an aqueous solution of iron(II) sulfate. At first, a white flocculent precipitate forms and gradually disappears. The mixture is then heated. The precipitate reappears. It is further observed that those portions of the precipitate exposed to air gradually become blue or even black.

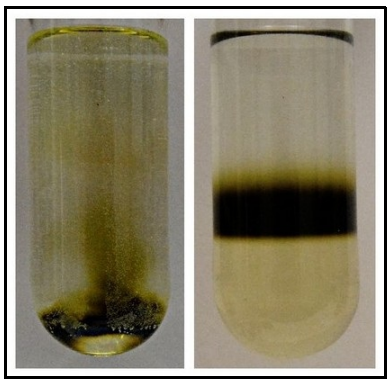


Figure 123

- A wide test tube is charged with a mixture of iron(II) sulfate solution and potassium nitrate solution. Two cubic centimeters of concentrated sulfuric acid are then allowed to flow down the wall of the tube so that the acid settles at the bottom. Finally, a small agglomerate of potassium nitrate crystals, approximately the size of a pea, is dropped into the mixture. The crystals react with the sulfuric acid to generate nitric acid. As a result of a complex reaction, a brown plume gradually develops, resembling the cloud rising from the summit of a volcano. As time passes, three distinct layers become visible within the tube, including a nearly black ring that slowly travels upward through the liquid. Depending upon the height of the liquid column, this ring may require two or three days to reach the top, where it finally disappears completely. Nothing then remains except a perfectly transparent yellowish liquid (Figure 123).

- A fairly concentrated iron(II) sulfate solution is prepared and treated first with nitric acid and then slowly with concentrated sulfuric acid. Nitric oxide is evolved and the iron(II) sulfate is converted into iron(III) sulfate. Verification may be carried out with sodium hydroxide solution, which now produces a red precipitate instead of the green precipitate obtained initially. Confirmation may also be obtained with a very dilute potassium thiocyanate solution, which develops the characteristic blood-red coloration.

- A solution of potassium permanganate is added gradually to an iron(II) sulfate solution. The liquid becomes yellow owing to the formation of iron(III) sulfate.

- Iron(II) hydroxide is first precipitated from iron(II) sulfate by addition of sodium hydroxide solution. The precipitate, initially whitish-green, gradually becomes green. It is stirred thoroughly and contact with air is minimized by maintaining a carbon dioxide atmosphere, closing the vessel, and allowing the precipitate to settle. Once the precipitate has settled, the supernatant liquid is removed. The precipitate is then dissolved in a hot citric acid solution. A beautiful green solution of iron(II) citrate is obtained.

- A tannin solution is added to a freshly prepared iron(II) sulfate solution. Nothing happens. Air is then bubbled through the mixture. A blue coloration appears. This explains why certain old inks darkened with age: increasing amounts of iron tannate gradually became fixed within the writing.

- Commercial iron sulfide, generally sold in cylindrical pieces, is always impure. The following curious experiment may be performed with it. A large airtight jar, such as those commonly used for preserving jam, is charged with a cylinder of iron sulfide together with a small open vial containing water. The jar is sealed so that the atmosphere within gradually becomes humid. After a sufficiently long period, the iron sulfide acquires the same yellow-orange coloration that iron(II) sulfate develops rather rapidly when exposed to air.

- A piece of iron sulfide is allowed to digest for a long time in very slightly diluted acetic acid. Over the course of several days, the liquid becomes increasingly red owing to the formation of iron acetate. The reaction proceeds much more rapidly when heated. If, after several days, the liquid is boiled, its color changes from a beautiful ruby red to a dark brick red owing to the formation of a basic acetate. Iron acetate solution does not keep well in any case, and no attempt should be made to crystallize it

- A sodium hydroxide solution is added gradually to an aqueous solution of iron(III) chloride. An abundant brick-red flocculent precipitate of iron(III) hydroxide immediately forms. A little glycerol is added to an aqueous iron(III) chloride solution and the mixture is stirred until homogeneous. Sodium hydroxide solution is then added. Instead of a precipitate, a homogeneous brick-red coloration is obtained. If hydrogen sulfide is subsequently bubbled through the liquid, a green precipitate appears. Had an alkaline sulfide been added instead, a green-black precipitate would have formed rapidly. The addition of glycerol likewise modifies the precipitates produced by alkaline hydroxides in other mineral solutions, including cobalt and nickel salts.

- A solution of sodium or potassium carbonate is added to an iron(III) chloride solution. A brick-red precipitate immediately appears. This is not ferric carbonate, which is unstable, but iron(III) hydroxide formed through decomposition of the carbonate, accompanied by the evolution of a little carbon dioxide.
The same observation applies to aluminum carbonate, which will be discussed later.

- A sodium bicarbonate solution is added to an iron(III) chloride solution. A brick-colored precipitate appears together with the evolution of carbon dioxide. The gas evolution becomes more vigorous and the precipitate darkens upon heating. A few drops of hydrochloric acid restore a clear yellow solution.

- A solution of ammonium phosphate is added to an iron(III) chloride solution. A brownish-yellow precipitate is formed.

- Add a ferric chloride solution to a sodium thiosulfate solution. A purple coloration appears but disappears rather quickly.

- Sulfurous acid is added to an iron(III) chloride solution. A color change is observed. The precipitate subsequently produced by sodium hydroxide is not greenish but rather black.

- An iron(III) chloride solution is placed in a beaker standing on a magnetic stirrer. Finely powdered calcium carbonate is added gradually. The liquid foams vigorously and changes color. Eventually it thickens into a gel-like mass before becoming fluid once more. Some investigators believe that a composition of this type, suitably modified, may lie at the origin of the famous *Miracle of Saint Januarius* in Naples, where the supposedly dried blood preserved in a sealed ampoule occasionally liquefies during religious ceremonies in which the ampoule is shaken. The formulation they propose is as follows: Dissolve 25 g of iron(III) chloride in 100 mL of water and add 10 g of calcium carbonate gradually.Allow the mixture to digest for four days, concentrate it by evaporation until the volume again reaches 100 mL, and add 1.7 g of sodium chloride. According to these authors, the solution gels within about one hour. I must confess that I attempted the experiment without obtaining this result. The hypothesis of a thixotropic gel appears to me an excellent explanation of the "miracle," but its exact composition remains to be determined.

- Place one drop of iron(III) chloride solution in the palm of one hand and one drop of potassium thiocyanate solution in the palm of the other. Bring the hands together in the attitude of prayer and then separate them. Bloody stigmata suddenly appear. This simple trick has occasionally been used to deceive the credulous. The appearance of the "wounds" may be enhanced by adding a little glycerol to the solutions.

- One or two drops of ammonium thiocyanate solution are added to a dilute iron(III) chloride solution. The liquid immediately develops a beautiful blood-red coloration. Two drops of this red solution are then transferred to a test tube containing at least 10 mL of ether. After agitation, the red color passes into the ether, while a whitish or yellowish droplet remains at the bottom of the tube. The experiment should not be performed by adding ether directly to the original red solution, because under those conditions the contents appear homogeneous. A much larger volume of ether would then be required to demonstrate the transfer of the red compound into the organic phase.

- A very dilute iron(III) chloride solution is prepared, sufficiently dilute to be perfectly colorless. A trace of potassium ferricyanide is added, followed by a single drop of hydrogen peroxide. Immediately, the liquid develops a beautiful blue coloration that sometimes passes through green. Success is assured only when very dilute solutions are employed.

- The following interesting experiment was reported on page 1276 of Volume LXXV of the *Comptes Rendus de l'Académie des Sciences* (Paris, 1872). A little solution of an iron salt, such as iron(III) chloride, is placed in a test tube. A few drops of sodium sulfide solution are then added. A black precipitate forms. Sulfurous acid is subsequently added. The precipitate assumes a whitish-yellow coloration and may disappear completely if a sufficient quantity of the acidic solution is employed. Other freshly precipitated metallic sulfides behave similarly, although the color change is particularly striking with iron salts. In reality, a complex sequence of reactions takes place. Sulfurous acid first produces a sulfite together with hydrogen sulfide. The latter reacts with sulfurous acid to form sulfur, which in turn converts the sulfite into thiosulfate. The reaction therefore depends upon whether the sulfite formed is soluble, since sulfur acts only upon soluble sulfites.

- Limewater added to an iron(III) chloride solution causes the liquid to become darker and cloudy owing to the formation of a scarcely visible precipitate of calcium ferrite. This precipitate disappears upon addition of a few drops of sulfuric acid.

- If sodium thiosulfate solution is added to iron(III) chloride solution, an extraordinarily dark red coloration appears instantly, so dark that it may seem black. Within ten to thirty seconds, however, the color changes completely and becomes yellow. If the solution is heated, a precipitate forms. After settling, this precipitate is found to be yellow-orange in color.

- A very dilute iron(III) chloride solution is prepared and divided equally between two test tubes. The first is heated to boiling. As the temperature rises, the liquid changes first to a dirty yellow and then to red. It is allowed to cool to room temperature, after which potassium ferrocyanide solution is added slowly. A blue coloration appears but rapidly changes to green. In contrast, the same ferrocyanide solution added to the unheated sample produces only an intense blue coloration.

- Iron(III) chloride solution is mixed with potassium ferrocyanide solution. Prussian Blue is formed. Oxalic acid solution and gum arabic solution are then added. A genuine writing ink is obtained.

- Oxalic acid solution added to iron(III) chloride solution produces a yellow precipitate of iron oxalate.

- A tannin solution added directly to iron(III) chloride solution produces a blue-black coloration.

- Addition of sodium thiosulfate solution to iron(III) chloride solution yields a violet precipitate that disappears slowly in the cold and rapidly upon heating.

- Mix an iron(III) chloride solution with a fairly concentrated calcium chloride solution, then add potassium hydroxide. A chamois-yellow precipitate of calcium ferrite forms and gradually becomes white, provided that contact with atmospheric carbon dioxide is prevented.

- Slowly add a calcium fluoride solution to an iron(III) chloride solution. A rust-colored precipitate is obtained. It dissolves in an excess of fluoride or becomes darker upon heating.

- Add a little acetic acid to a dilute iron(III) chloride solution. A red coloration appears owing to the formation of iron acetate. If hydrochloric acid is then added, the coloration disappears.

- Add a solution of sodium or potassium acetate to an iron(III) chloride solution. A red coloration of iron(III) acetate is obtained. If hydrochloric acid is then added, the color changes to yellow.
If, instead, the iron(III) acetate is heated to near boiling, the color changes and becomes more intensely red as a basic acetate forms, while acetic acid is evolved. A drop of sulfuric acid modifies the reaction further, producing a yellow basic iron(III) acetate.
If a little copper sulfate is added to the original iron(III) acetate solution, the iron precipitates as the hydroxide upon boiling.
Instead of beginning with an alkali acetate, lead acetate or copper acetate may be used, for example. The reactions are similar, but less clearly visible because of the blue color of the copper salt and because hydrochloric acid produces a yellow precipitate.

- Phenol water is added gradually to a dilute, barely yellow iron(III) chloride solution until a violet solution is obtained. A few drops of lactic acid are then added. The solution becomes golden yellow. The iron(III) chloride–phenol water mixture is in fact Uffelmann's reagent for lactic acid.

- Prepare a dilute iron(III) chloride solution. Add ethyl alcohol containing three or four drops of clove oil (eugenol). The color changes from blue to green and then, after one or two minutes, to yellow.

- Prepare two iron(III) chloride solutions, one in water and the other in ethyl alcohol. Separately, prepare a solution of phenol in ethyl alcohol. When the two alcoholic solutions are mixed, the coloration obtained is clearly different from that produced when the aqueous iron(III) chloride solution is mixed with the alcoholic phenol solution.

- Mix an aqueous or alcoholic solution of benzoic acid with an iron(III) chloride

solution. A pink, red, or yellowish precipitate forms, depending upon the concentrations employed. Add ether, shake vigorously, and allow the mixture to stand. The precipitate dissolves in the upper ether layer, which retains its coloration. If a saturated solution of benzoic acid, which is only slightly soluble in water, is used and a moderately concentrated iron(III) chloride solution followed by hydrogen peroxide is added, a violet coloration is obtained. If, on the other hand, a more concentrated iron(III) chloride solution is added followed by ether, the milky precipitate dissolves.

- Add a pyrogallol solution to a dilute iron(III) chloride solution. A blue coloration is obtained. If the same quantity of pyrogallol is added to a more concentrated iron(III) chloride solution, the blue coloration rapidly changes to red.

- Prepare a catechol solution and add it to a dilute iron(III) chloride solution. A green coloration is obtained, which changes to red upon addition of sodium hydroxide.

- Prepare an aqueous solution of salicylic acid, without concern if some of the acid remains undissolved. Add an aqueous iron(III) chloride solution. The liquid immediately becomes violet. Divide this solution into three portions. Add a little lactic acid to the first. The liquid becomes completely clear and golden yellow. Add an oxalic acid solution to the second. A perfectly clear yellow liquid is likewise obtained. Add dilute ammonia to the third. A red-orange liquid is obtained.
If the same operations are carried out in parallel using phenol water instead of a salicylic acid solution, similar results are obtained, with slight variations in color intensity owing to differences in the quantities and concentrations employed.
Most of these colorations are caused by extremely fine precipitates that gradually aggregate and settle at the bottom of the vessel.

Copper Salts (I) and (II)

- A little copper oxide is placed in a test tube and covered with ammonia solution. The tube is shaken from time to time. Gradually, the liquid acquires a blue coloration (Figure 124).

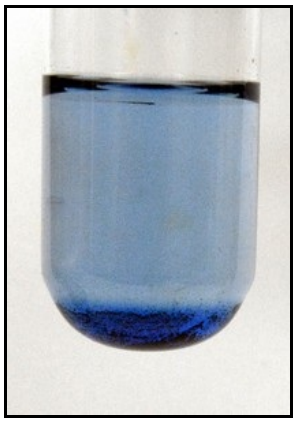


Figure 124

- If a zinc strip is placed in hydrochloric acid containing a very small amount of copper sulfate, the zinc reacts more rapidly. If, however, the zinc is placed directly in a copper sulfate solution and the acid is then added, the mixture soon becomes green. Hydrogen is evolved and, as the zinc disappears, finely divided copper is produced.

- A quantity of sodium chloride is placed in a porcelain mortar, followed by a larger quantity of copper sulfate. The mixture is ground until it becomes a fine powder. Ethyl alcohol is then added. The color, previously light blue, changes to green. Grinding is continued, after which the

mixture is transferred to a tall, well-stoppered bottle and allowed to settle. The green color alone demonstrates that copper(II) chloride has been formed. Since copper sulfate is not soluble in alcohol, the excess of this substance settles to the bottom.
Two test tubes are then prepared. One-third of the first is filled with the alcoholic solution of copper(II) chloride, while one-third of the second is filled with an aqueous solution of the same chloride. A small ball of aluminum foil is dropped into each test tube. In the alcoholic solution, nothing happens. In the aqueous solution, however, a vigorous effervescence occurs. If a flame is brought near the mouth of the tube, the escaping gas burns intermittently with the characteristic barking sound of hydrogen. A large quantity of copper is deposited and the test tube becomes very hot. If a little water is added to the alcoholic solution, the color changes from green to blue and small copper spots gradually appear upon the aluminum ball.

- If aluminum powder is projected into a fairly concentrated aqueous solution of copper(II) chloride, a vigorous and sometimes dangerous effervescence occurs. Aluminum oxychloride is formed while red copper floats in the liquid.

- A magnesium strip is placed in an alcoholic solution of copper(II) chloride. Gas is evolved and the strip becomes coated with a dark film. After forty-eight hours, the liquid, initially a beautiful green, is completely decolorized and the strip is covered with a green and red compound.

- Copper(II) chloride dissolves in aceton to give a rather dark, dirty yellow-green solution. If a zinc strip is introduced into this solution and the vessel is stoppered, the zinc gradually blackens. After about forty-eight hours, the liquid acquires a beautiful grass-green color. During the following days, the walls of the vessel become coated with a greenish layer while the zinc strip turns completely black.

- A sufficiently concentrated copper(II) chloride solution, green in color, is prepared and divided between three test tubes. Water is added to the first. The solution immediately becomes blue. Water is likewise added to the second test tube, followed by hydrochloric acid. The blue solution immediately changes to emerald green. In the third test tube, water is first added and then solid potassium chloride. Here again, the solution turns from blue to green.

- Concentrated hydrochloric acid is added dropwise to a copper(II) sulfate solution stirred at moderate speed by a magnetic stirrer. At each point where a drop meets the liquid, a yellow spot appears instantaneously and then disappears. Gradually, the entire solution assumes a beautiful emerald-green color, then a lighter green, and finally yellow.

- Copper sulfate is dissolved in concentrated hydrochloric acid. A yellowish-green solution is obtained. A layer approximately 1 cm deep is placed in a 500 mL bottle standing on a magnetic stirrer. Water is then added gradually. The liquid first becomes emerald green and then turns blue.

- If an alcoholic solution of copper(II) chloride is ignited, the flame varies from blue to orange-red and is bordered by green. At times, this characteristic green coloration of copper becomes very intense and produces a remarkably luminous flame (Figure 125).

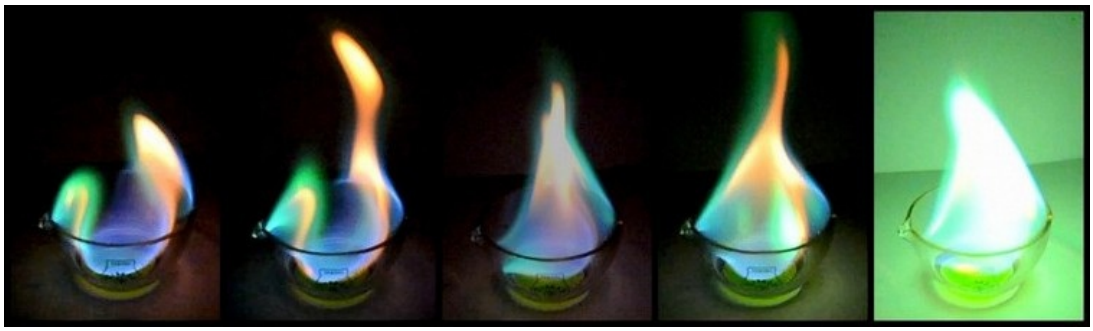


Figure 125

- A few grains of sodium dichloroisocyanurate are placed in a test tube and a few drops of copper sulfate solution are added. The grains immediately acquire a violet coloration.

- A sodium nitrite solution is added to a copper(II) sulfate solution. The blue solution immediately turns emerald green.

- A solution of sodium or potassium cyanide is added slowly to a copper(II) sulfate solution. A yellow precipitate is formed. After settling, it appears more yellowish than truly yellow.

- A fairly concentrated copper(II) chloride solution is placed in a test tube. Two drops of mercury are added and the mixture is shaken vigorously. The liquid becomes cloudy and, little by little, the mercury disappears. A white solid chloride and a black mass are formed.

- A concentrated copper(II) chloride solution is placed in a test tube. A small piece of phosphorus is introduced and the mixture is shaken vigorously. Copper phosphide, copper metal, phosphoric acid, and hydrochloric acid are formed.

- Copper sulfate solution is added slowly to bleach. A greenish-yellow precipitate is formed together with the evolution of sulfur dioxide and the appearance of copper grains. If a little nitric acid is then added, the copper reacts, producing a small quantity of red nitrous fumes, while the precipitate dissolves.

- A greenish-blue solution of copper(II) chloride is converted into colorless copper(I) chloride by treatment with tin(II) chloride in hydrochloric acid solution. Although white copper(I) chloride is insoluble in water, it dissolves in water containing hydrochloric acid and gradually acquires color upon exposure to air.

- A mixture of copper sulfate solution and sulfurous acid reacts with potassium

iodide solution to produce a brown precipitate. Upon heating, iodine is lost and the precipitate is converted into cuprous iodide, CuI.

- A solution of copper(II) sulfate or copper(II) chloride gives, with sodium sulfite solution, a precipitate of a characteristic dull olive-brown color.

- A sodium silicate solution added to a blue copper sulfate solution produces a beautiful blue precipitate.

- Sodium phosphate solution added to copper sulfate solution immediately produces a blue-green precipitate.

- Potassium iodide solution added to copper acetate solution immediately forms a precipitate of copper iodide with a dull olive-brown coloration.

- Oxalic acid solution added to copper(II) chloride solution immediately yields a fine white precipitate of copper oxalate. If the liquid is decanted and hydrochloric acid is added to the white precipitate, the latter disappears and a beautiful green solution is obtained. Addition of water to this green solution restores the familiar blue coloration

- Three test tubes are prepared. A fairly dilute copper sulfate solution is placed in the first, a moderately concentrated lead nitrate solution in the second, and water containing a few drops of phenolphthalein in the third. A moderately concentrated ammonia solution is then added successively to each of the three test tubes, followed by vigorous agitation. The result is... the French flag.

- Copper(II) hydroxide is first prepared by adding sodium hydroxide solution to copper sulfate solution. Hydrogen peroxide that is not excessively concentrated is then added. Oxygen is evolved and a black copper oxide appears, accompanied by a considerable rise in temperature. The liquid often overflows from the test tube.

- Prepare a precipitate of copper hydroxide by adding sodium hydroxide solution to copper sulfate solution. Mix the colloidal precipitate thoroughly and then add chlorine water. The blue color changes to dark green. Repeat the experiment, but this time add sodium thiosulfate solution instead of chlorine water. The precipitate dissolves. Repeat the experiment once more and heat the precipitate obtained initially. Black grains of copper oxide form rapidly. Addition of hydrochloric acid then produces a transparent green solution.

- Copper sulfate solution forms, with potassium hydroxide or sodium hydroxide solution, a hydroxide precipitate that dissolves in a large excess of reagent. If a little glycerol is mixed with the copper sulfate solution before the alkali is added, the precipitate no longer appears and a beautiful sky-blue solution is obtained directly. A soluble copper glycerolate has in fact been formed. A similar reaction may be obtained by substituting tartaric acid for glycerol.

If the blue liquid containing potassium hydroxide and glycerol is heated, a precipitate of a beautiful brick-red color is formed. The reaction is rather similar to that used for the identification of glucose with Fehling's solution.

- Two solutions are prepared, each in a 100 mL ISO bottle placed on a magnetic stirrer. The first consists of 6.5 g of copper sulfate dissolved in 20 mL of water. The second consists of 6.5 g of ammonium persulfate dissolved in 15 g of 25% ammonia. While an ice-water bath is being prepared, both bottles are placed in a freezer. After five full minutes, they are removed. The persulfate solution is poured into a 100 mL beaker standing in the cooling bath, after which the copper sulfate solution is added dropwise. From the outset, the cooling bath should itself be placed on a magnetic stirrer and the mixture stirred gently throughout the addition of the two solutions. A gradual thickening of the liquid is observed. When the addition is complete, stirring is continued for one to five minutes. The beaker is then removed from the cooling bath and allowed to stand. A blue deposit settles to the bottom. A Büchner funnel mounted on a filter flask is prepared, and the liquid together with the solid is poured onto filter paper previously placed in the funnel.The material is washed with aceton while suction is maintained. Washing is complete when the aceton runs colorless. The filter paper is then removed and placed on perforated porcelain to facilitate drying. Copper(II) tetraammine sulfate is thus obtained. On contact with air, this substance tends to change gradually. It should therefore be recovered as rapidly and as dry as possible, for example by placing the porcelain on a radiator and stirring the product frequently. An infrared lamp positioned at a reasonable distance may also be used, as may a more elaborate drying device such as the epiradiator described previously. One of the properties of this substance is that it deflagrates when struck by the flame of a blowtorch. It is therefore often described as explosive, although this is probably an exaggeration, since a quantity no larger than a split pea produces only a faintly audible pop.

- A concentrated copper sulfate solution is prepared and ammonia is added until the precipitate that first appears has completely redissolved. A magnificent deep-blue solution is obtained. This solution was formerly known as Celestial Water. This color disappears rapidly upon addition of hydrochloric or sulfuric acid.
A more spectacular way of carrying out the experiment is to begin with a very dilute copper salt solution, so dilute that the liquid is colorless. When ammonia is added, the solution turns blue without any precipitate forming, since the ammonia is necessarily present in excess. This beautiful blue color then disappears upon addition of acid. If ethyl alcohol is added instead of acid, a mauve-violet precipitate appears. This time, the compound formed is a complex corresponding to the formula $[Cu(NH_3)_4]SO_4 \cdot H_2O$, known as tetraamminecopper(II) sulfate. No attempt should be made to dry this salt over a flame, since it is explosive in nature.
Some authors state, and I believe correctly, that the tetraamminecopper ions $Cu(NH_3)_4$ obtained by the action of ammonia on copper sulfate are unable to dissolve cotton because they are associated with sulfate ions, SO_4.
The same ions obtained by reacting ammonia with copper carbonate, or ammonia and air with metallic copper, would, on the other hand, be capable of dissolving

cellulose. Pharmaceutical cotton wool made of 100% cotton should be used for this experiment. I must admit that I attempted it without much success, leaving the cotton in contact with the solution for forty-eight hours. I did obtain a liquid somewhat more viscous than it had been initially, but when I added it drop by drop to a dilute sulfuric acid solution, instead of obtaining a smooth blue fiber, I obtained only small bluish flakes.

- Prepare a pale sky-blue precipitate of copper(II) hydroxide by adding sodium hydroxide to a copper(II) sulfate solution. Wash the precipitate thoroughly and then dissolve it in ammonia. The resulting beautiful blue liquid is Schweitzer's reagent, prepared by a rapid method. Most chemistry texts state that it has the property of dissolving genuine cotton and silk. This is only partly true, since specific conditions must be met and, in particular, a little copper chloride must be added (Launer & Wilson, "*Preparing Cuprammonium Solvent…*," *Analytical Chemistry*, 1950, 22(3), pp. 455–458).

- A little glucose is added to Celestial Water obtained by the action of ammonia on a copper(II) salt, and the liquid is heated. Decolorization occurs.

- Scheele's Green was once a widely used pigment for both fabrics and wallpaper. It caused many cases of poisoning, however, because it was an arsenic-based compound. Here is a simple way of preparing it. A few drops of copper sulfate solution are placed in a test tube, and water is added until a lightly colored solution is obtained. A little ammonia is then added to produce an intensely blue solution. This solution is diluted considerably once again, after which a very small quantity of arsenic trioxide is added and the mixture is heated. The liquid then changes color. As soon as boiling begins, heating is stopped and the mixture is allowed to stand. A beautiful green flocculent precipitate can then be seen descending to the bottom of the test tube. The more concentrated the ammonia solution, the darker the pigment obtained.

Figure 126

Zinc Salts

- Place zinc, or preferably zinc powder, in a freshly prepared solution of H_2SO_3. A yellow coloration is obtained which soon disappears while a deposit of colloidal sulfur forms. This deposit may itself later tend to disappear. Yellow hydrosulfurous acid is formed first, followed by a soluble zinc hyposulfite with deposition of sulfur. (Already mentioned, in a somewhat different form, on page 180.)

- Into a solution of zinc sulfate, slowly pour a solution of sodium hydroxide while stirring. A white hydroxide precipitate first forms. The solution then clears and becomes transparent because sodium zincate has been formed. Next, add H_2SO_4 drop by drop. The precipitate reappears and then disappears once again. A hydroxide precipitate has in fact formed again and has then been transformed into sulfate. A similar experiment will be described below with an aluminum salt.

- In a porcelain mortar, crush together 14 g of zinc sulfate and 11 g of KBr. Liquefaction gradually occurs and zinc bromide is formed. Unlike most of the reactions described in the present chapter, this one therefore does not require any external addition of water in order to obtain liquefaction of the substance.

- Pour a little zinc oxide into concentrated ammonia and place the mixture on a magnetic stirrer. The gradual disappearance of the white coloration is observed. Zinc ammoniate is formed.

- Into a solution of zinc sulfate, pour a solution of recently prepared ammonium thiocarbonate. A pale yellowish-white precipitate forms. Allow it to dry. It becomes reddish.

Lead Salts

- Pour a solution of HI into a solution of lead acetate. An orange-yellow precipitate of lead iodide is formed.

- Into an aqueous solution of lead acetate, pour an aqueous solution of potassium iodide. A yellow precipitate of lead iodide forms. Pour an aqueous solution of sodium hyposulfite over it. The precipitate immediately disappears and the liquid becomes clear and colorless again.

- Prepare lead sulfide by means of H_2S + lead acetate. Pour H_2O_2 onto it. Oxygen is evolved and the black sulfide is transformed into white sulfate.

- Into a solution of lead nitrate or lead acetate, slowly allow sodium hypochlorite (bleach) to run in. A white precipitate first forms, then orange, then sienna-colored, and finally, with time, brown. The transformation is very rapid if the mixture is heated. Ultimately, lead dioxide is formed.

- Yellow lead tetrachloride, PbCl4, can be obtained simply by dissolving PbO_2 in cold HCl.

- Prepare an aqueous solution of 7.5 g of sodium perborate and a solution of 9.5 g of lead acetate. Each of these two solutions should be prepared in a minimum amount of water that has previously been boiled and then allowed to cool in a tightly stoppered bottle filled up to the neck. When both solutions are ready for use, pour one into the other. A lemon-yellow precipitate of lead perborate, $Pb(BO_3)_2 \cdot H_2O$, is obtained immediately, or sometimes after a short time. It may be allowed to settle and then washed with alcohol followed by ether if one wishes to preserve it.

- Prepare a concentrated solution of lead acetate. Add formic acid drop by drop until present in excess. A white precipitate of lead formate forms.

- Prepare a moderately concentrated solution of lead acetate. Pour one quarter of its volume into each of four beakers containing potassium dichromate solutions. The first solution should be of medium concentration. The second should be identical but with a little calcium hydroxide added. The third should be more dilute, and the fourth should be brought to a boil. It will be observed that the precipitates have distinctly different colors (Figure 127).

Figure 127

Figure 128

- A similar experiment may be carried out with potassium chromate. A lumpy canary-yellow precipitate forms and settles rapidly. Divide this precipitate into two portions. Pour a concentrated solution of potassium hydroxide onto the first. The precipitate dissolves completely, producing a canary-yellow liquid. Pour concentrated ammonia onto the second. A red precipitate of basic lead chromate forms and gradually changes toward a brick-orange color (Figure 128). In order to demonstrate this effect clearly, it is preferable in this particular case to begin with a rather dilute solution of lead acetate.

- A piece of white cotton is dipped into an aqueous solution of lead acetate and then, without being wrung out, into a

solution of potassium dichromate. Stir briefly, rinse thoroughly with water, and allow to dry. The cotton is now colored yellow.

- Into an aqueous solution of lead sulfate, pour an aqueous solution of ammonium sulfocyanide (thiocyanate). A white precipitate forms. If a little hydrogen is bubbled through this liquid, a black precipitate immediately forms and the pH becomes acidic owing to the formation of thiocyanic acid.

Tin Salts

- Place a small amount of tin(II) chloride in a test tube and add a little water. A liquid somewhat resembling milk is formed. Finally, add a small quantity of a gold salt. The liquid immediately assumes a mauve coloration which, depending on the concentration of the reagents present, may sometimes become very dark.

- Take two test tubes and place 3 cm of concentrated hydrochloric acid in each. Add a small amount of arsenious oxide to the first and a small amount of tin chloride to the second. Shake both test tubes to dissolve the solids and then pour the contents of the second into the first. Depending on the amount of arsenious oxide added, the liquid becomes yellow, then brown, and finally black. A deposit of arsenic forms.

- Add a little stannous chloride to an acidified solution of ammonium molybdate. The color turns blue.

- Add a small amount of powdered tin(II) chloride to a solution of selenious acid and shake. A red precipitate forms immediately.

Nickel Salts

- To a solution of a nickel salt, such as nickel sulfate, add a solution of NaOH. A beautiful apple-green precipitate forms. If bromine water is added, it becomes completely black.
If, instead of bromine water, concentrated ammonia is added to the precipitate, the latter dissolves to give a clear liquid of a beautiful blue color, similar to the sky-blue solution obtained when copper hydroxide is dissolved in an excess of ammonia.
Finally, if ammonium chloride and then NaOH are added directly to the original nickel salt solution, the clear blue liquid is obtained immediately without passing through the precipitation stage. Nickel hydroxide precipitate dissolves readily only in an acid or in an ammonium salt solution containing ammonia.

- Pour an aqueous solution of sodium silicate into a green solution of nickel sulfate. A precipitate of a beautiful light green color is obtained.

- In a large test tube, place a few drops of a green solution of nickel sulfate or nickel

chloride. Gradually add ammonia until a perfectly clear blue liquid is obtained. Then add distilled water until the blue coloration disappears. Finally, add drop by drop a solution of an alkaline thiocarbonate diluted so that it is only faintly yellow. A precipitate forms which gradually acquires a currant-red color. The presence of polysulfides or a monosulfide in the thiocarbonate solution may greatly influence the color of the precipitate, which may then be yellow or brown (polysulfides) or black (sulfide). For this reason, one should try to work with a thiocarbonate solution that has just been prepared, since this solution does not keep and tends precisely to develop various impurities.

- Into a test tube, pour a beautiful green solution of nickel sulfate to a depth of 3 to 4 cm. Add a concentrated solution of sodium cyanide drop by drop. A pale greenish-white precipitate first forms and then redissolves in an excess of reagent, giving a yellow solution. The test tube then contains a tetracyanonickelate(II) complex. Next, place a piece of zinc and a few grains of NaOH into the tube. A red coloration gradually appears at the bottom of the test tube. A nickel(I) complex is formed. If a little of this red liquid is withdrawn with a pipette and diluted H_2SO_4 is added, a yellow precipitate is obtained. If H_2O_2 is then added, a white precipitate forms.
If a few drops of sodium hypochlorite are added to the original yellow solution, the liquid becomes black owing to the formation of another complex precipitate.

- Pour a solution of oxalic acid into a solution of a soluble nickel salt (for example, nickel sulfate). At first, nothing happens. However, within a few hours, a green deposit of oxalate forms while the liquid becomes colorless. If this liquid is poured off and replaced with ammonia, nothing happens at first; then, gradually, the deposit disappears to form a blue solution.

Aluminum and Magnesium Salts

- Begin by pouring a solution of sodium hydroxide into a solution of aluminum sulfate. A milky white precipitate forms which, upon addition of an excess of hydroxide, is transformed into a clear solution of sodium aluminate. Add HCl (or H_2SO_4) drop by drop. The hydroxide precipitate reappears and then disappears once again through the formation of a solution of aluminum chloride (or sulfate). A rather similar experiment was mentioned above with a zinc salt.

- In a flask, prepare an aqueous solution of aluminum sulfate in which a dye such as methylene blue has been dissolved. Then add a solution of sodium hydroxide, which forms a precipitate of alumina. Mix thoroughly and filter. A kind of colored jelly remains on the filter, consisting of alumina that has retained the dye. If too much dye was not added initially, the filtrate runs through colorless. Alumina has the property of retaining dyes within itself, and this property is used in certain textile dyeing processes.

- If a solution of potassium carbonate is poured into a solution of aluminum sulfate, a milky precipitate of aluminum hydroxide (alumina) is immediately obtained because aluminum carbonate is unstable and is instantly transformed into hydroxide upon contact with water (the same observation was made earlier concerning ferric carbonate).

- Take three beakers. Into the first, pour a saturated solution of ordinary potash alum. Then slowly add ammonia while stirring. A gelatinous precipitate of alumina forms. Transfer one third of this precipitate into the second beaker and another third into the third beaker. Into the second, slowly add H_2SO_4. The precipitate disappears. Into the third, add ammonia. The precipitate also disappears, but more slowly. This experiment shows that alumina combines equally well with acids and bases.

- In one flask prepare an aqueous solution of lead acetate. In another, prepare an aqueous solution of aluminum sulfate. Then mix the two solutions. A white precipitate of lead sulfate is obtained while the clear liquid contains aluminum acetate. Bring the mixture to a boil in order to obtain more rapid settling. After partial cooling, settling is complete. Decant the clear liquid and add a little ammonia. A gelatinous precipitate of alumina forms.

- Pour a little potassium ferrocyanide solution into a solution of aluminum sulfate. Nothing appears to happen. Nevertheless, after a fairly long time, a fine white precipitate is observed to have settled.

- In a crystallizing dish (or any other flat-bottomed glass vessel such as a Petri dish), spread a thin layer of magnesium oxide. Do the same in a second vessel, using magnesium hydroxide this time. Using a spray bottle, spray the entire surface of these substances with a concentrated solution of calcium chloride. After a few hours, it will be observed that the powder in the first vessel remains soaked, whereas that in the second has hardened and set into a solid mass like plaster. Hot water, however, dissolves it.

- Prepare a basic solution of sodium aluminate by digesting aluminum in a solution of sodium hydroxide. Allow sufficient time and heat from time to time if necessary to accelerate the reaction. When the solution reacts only very slightly with the aluminum, filter and dilute with water, then add HCl. An abundant mucilaginous precipitate of alumina immediately forms. Instead of HCl, add a solution of potassium dichromate. A very beautiful lemon-yellow precipitate is obtained.

- Magnesium salts and their precipitates are colorless or white. There is, however, one exception. Into a dilute solution of a magnesium salt, add a few drops of a freshly prepared KI solution followed by a few drops of sodium hypochlorite solution. A reddish-brown precipitate is obtained, although it is not really an ordinary compound. In fact, very finely divided magnesium hydroxide is formed and remains suspended while the iodine liberated from the KI becomes fixed to, without

combining with, the hydroxide particles. It should be noted that it is sometimes necessary to make the solution alkaline with a drop of NaOH and that sodium hypochlorite may be replaced by sodium hypobromite.

- Heat a liquid mixture consisting of a solution of magnesium chloride and a solution of calcium sulfide. A rotten-egg odor is evolved and the test tube becomes coated with sulfur. When the experiment is carried out with the two substances dry, only H_2S, $CaCl_2$, and $Mg(OH)_2$ are formed.

Cobalt Salts

- When placed in a flask with concentrated HCl, cobaltous oxide (CoO) reacts to some extent, since the liquid becomes blue. In the cold, it does not react with the other two common mineral acids: nitric and sulfuric acids. However, when placed in aqua regia, it gradually colors the liquid green.

- Pour concentrated HCl into a pink solution of cobalt chloride. The solution turns blue. After a long time, it tends to become pink again. If it is then heated, it turns blue once more.
Starting from a concentrated (red) solution of cobalt chloride, a green color is obtained. The cobalt chloride solution in HCl that turns blue upon heating has sometimes been called the "chemical thermometer." It keeps practically indefinitely in a tightly stoppered bottle.

- Dissolve cobalt chloride in aceton. A blue solution is obtained which gradually becomes lighter. When heated in a water bath, it regains its original blue color. This is another form of "chemical thermometer."

Dissolve a little cobalt chloride in water. The solution becomes pink. Likewise, dissolve a little of the same substance in absolute alcohol. The solution becomes blue. To this latter solution, add water drop by drop until a pale mauve color, intermediate between blue and pink, is obtained. Heat the liquid and it becomes blue again. Cool it and it becomes mauve again. This may be repeated a great many times because, depending on the temperature, water leaves or recombines with the salt, which consequently becomes blue or pink.

- If a dilute aqueous solution of a cobalt salt is treated slowly with a dilute aqueous solution of NaOH, a precipitate first forms that is blue and then turns green, sometimes passing through a dirty yellow color. However, I have also observed gray or pink colors. In fact, these successive shades depend greatly (as is often the case) on the concentration of each solution. If a few drops of H_2O_2 are then added, abundant oxygen is evolved and the entire liquid may become brown.

- An aqueous solution of cobalt chloride to which a little glycerin has been added, followed by a little aqueous NaOH solution, gives a blue liquid. In contrast, the same

solution without glycerin gives, with NaOH, a blue precipitate that rapidly turns green, then becomes gray in air and finally pink. This pink coloration is intensified by heat. If a little bromine water is poured onto this precipitate, it becomes black.

- Prepare a blue precipitate of cobalt hydroxide by adding a few drops of NaOH solution to an aqueous solution of cobalt chloride or cobalt nitrate. Then pour an aqueous solution of oxalic acid into the test tube containing the precipitate. The liquid returns to its original pink color. Had a drop of hydrogen peroxide been added instead of oxalic acid, the precipitate would have been transformed into brown-black cobalt sesquioxide with abundant foaming.

- To a solution of cobalt chloride, add dilute ammonia little by little. A blue precipitate forms. Then add concentrated ammonia. The blue precipitate dissolves in a yellow liquid owing to the formation of cobalt ammine complexes.

- Place a little cobaltous carbonate in a test tube. Pour a little HCl over it. The liquid effervesces and acquires a beautiful blue color. It is sometimes necessary to heat gently in order for this reaction to occur. Add water. The liquid takes on a pink-magenta color. Gradually add ammonia. The color then changes to a shade varying between melon-yellow and red, depending on the quantities and concentrations involved.

- If powdered cobalt carbonate is poured into a dilute solution of nitric acid, the mixture effervesces and slowly becomes red (cobalt nitrate solution). The reaction is accelerated by gentle heating.

- A solution of a cobalt salt mixed with a solution of ammonium carbonate gives a lilac precipitate which becomes mauve upon heating.

Pour 3 cm of cobalt(II) chloride solution into two test tubes. To the first, add a solution of sodium bicarbonate (hydrogen carbonate). A flocculent lilac precipitate forms. To the second, add a drop of hydrogen peroxide before adding the bicarbonate. In this case, a green-to-brown precipitate forms and the liquid foams strongly. This green precipitate is a cobaltic cobalticarbonate complex, $Co[Co(CO_3)_3$.

- Into a medium-sized test tube, pour a fairly concentrated solution of potassium carbonate and then, without excessive stirring, carefully add an aqueous solution of cobalt chloride. A lumpy precipitate forms whose color is not uniform (Figure 129).

- A solution of a cobalt salt mixed with a solution of oxalic acid gives a very fine white-pink precipitate which forms slowly.

- A solution of a cobalt salt mixed with a solution of an alkaline sulfide gives a black precipitate.

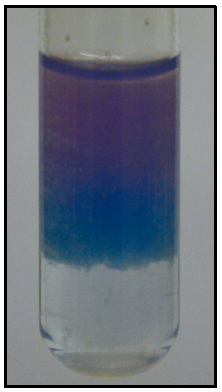


Figure 129

- A solution of a cobalt salt mixed with a solution of potassium ferrocyanide gives a green-gray precipitate.

- A solution of a cobalt salt mixed with a solution of potassium ferricyanide gives a red-brown precipitate.

- Add a solution of cobalt chloride drop by drop to a solution of sodium phosphate. The liquid first acquires a beautiful blue color and then, slowly, a fine indigo-blue precipitate of cobalt phosphate forms.

- Into a test tube, pour a solution of cobalt chloride and then a solution of sodium cyanide. A dirty brown-yellow precipitate of cobalticyanide forms and dissolves in an excess of reagent to give a beautiful yellow or even green liquid, depending on the concentrations of the solutions. If heated, the liquid may become olive-yellow through the formation of a cobaltocyanuric complex.

- Add a little sodium hypobromite to a solution of a cobalt salt to which a little glycerin has been added. A goose-dropping-green precipitate is obtained.

- To a pink solution of cobalt chloride add a little acetic acid and then crystals of sodium nitrite. The solution gradually becomes blood-red while effervescing.

- A solution of cobalt(II) salt brought into contact with a solution of ammonium sulfocyanide gives a complex precipitate that may be brown, then green, and even blue-violet. It is soluble in an excess of reagent.

- If a solution of ammonium sulfocyanide is prepared in ethyl alcohol and a very small amount of a cobalt salt is added, a beautiful sky-blue coloration develops owing to the formation of anhydrous cobalt sulfocyanide. If a little water is added, the liquid becomes completely decolorized.
The same sulfocyanide may be obtained by using an aqueous solution of ammonium sulfocyanide and a solution of cobalt chloride in aceton.
A third method is as follows: add a little aniline to an aqueous solution of cobalt chloride, then add a solution of ammonium sulfocyanide. A sky-blue coloration is obtained which passes into the solvent.

- Into a pink-red solution of cobalt chloride, gradually add crystals of ammonium sulfocyanide. The liquid turns blue. Divide it into two portions. Add water to the first. The color changes to pink. To the second, add a previously prepared mixture of equal parts ether and amyl alcohol. A magnificent blue coloration is obtained.

- Place a little mercury(II) chloride in a test tube and add 3 to 4 cm of water above it. Heat to dissolve. Then add a few drops of sodium sulfocyanide and shake. The liquid remains colorless. Finally, add a solution of cobalt nitrate drop by drop. The color of the liquid gradually changes from lilac-pink to indigo and then to ultramarine blue. In some cases, a black deposit may appear at the bottom of the test

tube. The coloration persists, but if a little ethyl acetate is added, most of the blue passes into the upper immiscible layer, while only a very pale blue remains below.

- To a dilute solution of cobalt chloride add a little tartaric or citric acid, then add ammonia in excess. A first color change occurs. Then add a solution of potassium ferricyanide. The color changes from yellow to dark red, depending on the initial concentration. This is a very sensitive reaction for detecting the presence of cobalt in a saline solution.

- Into a solution of a cobalt salt, pour potassium nitrite acidified with a little acetic acid and heat very gently. The liquid immediately becomes yellow-orange and, if heating is continued, reddish fumes are evolved.

-Into a pink solution of cobalt chloride, pour an aqueous solution of sodium silicate. A beautiful lilac precipitate is obtained.

Barium, Cadmium, and Bismuth Salts

- Place a PVC beaker in the lid of a Petri dish whose diameter is only slightly larger than that of the beaker, while placing a few drops of water between the two. Then place equal parts of powdered ammonium chloride and powdered barium hydroxide into the beaker. Mix the two powders using a glass rod. Very quickly, they appear to become moist and then liquefy. If a thermometer is immersed in the beaker, it will be observed that the temperature rapidly falls to –20°C and may even reach nearly –30°C after one minute. The water placed between the beaker and the Petri dish lid freezes and the lid adheres to the beaker. Do not touch the coldest parts of the beaker because there is a risk of cold burns. Although expensive, this method can very well be used to obtain intense cold rapidly.

- In a small, tightly stoppered flask containing a Teflon-coated magnetic stir bar, place one spatulaful of barium peroxide, together with a mixture of half water and half carbon disulfide. Stopper the flask and place it on a magnetic stirrer. After only five minutes, a slight yellow coloration is observed. This gradually intensifies, passing through lemon-yellow and then sienna-yellow. A colored barium sulfide and sodium carbonate are formed.

- Into a solution of barium chloride, pour a solution of potassium hydroxide. A rather fine white precipitate is obtained. This precipitate is soluble in a large amount of water. Ammonia, used instead of potassium hydroxide, produces no precipitate.

- In a solution of barium chloride, a solution of ammonium carbonate or a solution of sodium phosphate both produce a white precipitate.

- An aqueous solution of oxalic acid or of an oxalate produces a white precipitate in a solution of barium chloride. This precipitate dissolves in HCl. If sufficient ammonia

is then added, the precipitate reappears.

- If a solution of potassium chromate is poured into a solution of barium chloride, a milky yellow precipitate used in painting is obtained.

- Into an aqueous solution of ammonium molybdate, pour an aqueous solution of barium chloride. A thick white precipitate of barium molybdate forms.

THE "IDEAL" PSEUDO-REAGENT FOR SULFATES

Solutions of sulfates, as well as sulfuric acid, produce a very abundant white precipitate in a solution of barium chloride. It is often said that this reaction is sufficient to identify sulfate ions. It is clear, however, in view of the preceding experiments, that this is not sufficient, or that considerable experience is required to distinguish, solely by appearance, the white precipitates of barium sulfate, phosphate, carbonate, oxalate, molybdate, and hydroxide.

- Pour baryta water into two large test tubes and then add an aqueous solution of potassium chromate to each. A lemon-yellow precipitate of barium chromate forms. Add a little concentrated HCl to the first test tube and a little concentrated HNO_3 to the second. In both test tubes, the precipitate disappears and is replaced by a beautiful deep yellow liquid. Then pour an ammonia solution into each test tube. The lemon-yellow precipitate reappears in both.

- When mixed with a solution of cadmium acetate, a solution of potassium ferrocyanide gives a yellowish-white precipitate, whereas a solution of potassium ferricyanide gives a dirty yellow precipitate.

- To a solution of a cadmium salt, add a solution of potassium sulfide or another alkaline sulfide. A lemon-yellow precipitate forms. This precipitate dissolves in hot H_2SO_4 or in an excess of HCl. It becomes red when heated and returns to yellow upon cooling.
If H2S is bubbled through the cadmium salt solution from the outset, the crimson-red variety is obtained directly. Upon heating, it becomes brick red.

- A solution of sodium or potassium hydroxide gives a white precipitate in a solution of cadmium acetate. This precipitate is not soluble in an excess of hydroxide.
Dilute ammonia also gives a white precipitate in a solution of cadmium acetate; however, it dissolves very rapidly in an excess of reagent.

- A solution of potassium carbonate or sodium carbonate gives a white precipitate in a solution of cadmium acetate. This precipitate is insoluble in an excess of carbonate.

- A solution of sodium phosphate gives a white precipitate in a solution of cadmium

acetate.

- Into a solution of bismuth nitrate, pour a solution of potassium chromate or potassium dichromate. A yellow precipitate is obtained which dissolves in HNO_3 to give a beautiful orange-colored liquid.

- Into a solution of bismuth nitrate, slowly pour a solution of NaOH. A white precipitate forms. If this precipitate is heated, it becomes yellow as $Bi(OH)_3$ is transformed into BiO(OH).

- Ammonium sulfide solution reacts with a solution of bismuth nitrate to form a black precipitate of bismuth sulfide, Bi_2S_3.

- Potassium iodide solution reacts with a solution of bismuth nitrate to form bismuth iodide, BiI_3, whose color may vary from orange to black, passing through brown depending on the concentrations of the two reagents.

- A solution of bismuth nitrate poured into a solution of potassium ferrocyanide gives a white precipitate.

- If a solution of tannic acid is poured into a solution of bismuth nitrate, a yellow precipitate is obtained.

Lithium, Strontium, and Cerium Salt

- If a little lithium carbonate is placed in a test tube and water is poured over it, it can be observed that the carbonate does not dissolve. If a very small amount of sulfuric acid is then added, effervescence occurs and the carbonate is transformed into sulfate, giving a colorless liquid.
The same thing occurs with HCl or HNO_3. This is the usual method of preparing certain lithium salts.

- Prepare a relatively concentrated solution of lithium chloride by gradually dissolving lithium carbonate in concentrated HCl diluted with an equal volume of water. Stop when the carbonate ceases to react and allow the mixture to settle. Pour a little of this solution into four test tubes, then dilute two of them with approximately twice their volume of water. Next, pour a little aqueous potassium phosphate solution into two of the test tubes containing the lithium salt at two different concentrations, and into the other two test tubes pour a little aqueous potassium carbonate solution. With the concentrated lithium chloride solutions, a white precipitate may form immediately. Where no precipitate appears, it is sufficient to heat to boiling, or even before boiling, for a white cloudiness to develop. These are two reagents for lithium salts. The experiment should be carried out with a chloride or a sulfate because these salts are much more soluble in water than the carbonate and therefore allow more concentrated solutions to be obtained.

- Into a dilute solution of lithium chloride, allow a few drops of an aqueous silver nitrate solution to flow. The usual precipitate is formed, exhibiting the color changes in light characteristic of chlorides.

- Strontium carbonate is only slightly soluble in water, but it reacts readily with HCl to form a neutral solution of strontium chloride, $SrCl_2$.

- Place strontium chloride or strontium nitrate in a small dish with a little ethyl alcohol. Ignite the alcohol. In both cases it burns with a distinctly visible reddish flame envelope. Strontium salts are therefore used in colored fireworks.

- Prepare an aqueous solution of cerium sulfate by first slightly acidifying the water with H_2SO_4. At room temperature, a beautiful yellow liquid is thus obtained. Pour two or three centimeters of this solution into a series of five test tubes. To the first, add a few drops of NaOH solution, and to the second a few drops of dilute ammonia solution. In both cases, a white flocculent precipitate is obtained and the yellow color disappears. Into the third test tube, pour a few drops of sodium sulfocyanide solution. The liquid becomes colorless, but nothing more occurs. Into the fourth test tube, pour a few drops of sodium sulfide solution, Na_2S. A rather thick white precipitate first forms, then upon agitation becomes flocculent and yellowish. Into the last test tube, pour phenolated water. The liquid remains clear but gradually becomes brown, and a precipitate of that color may even slowly settle.
NOTE: The yellow aqueous solution of cerium sulfate may also be prepared without adding sulfuric acid by heating slightly. Not too much, however, because above a certain temperature the solubility of this salt in water decreases.

- If an aqueous solution of sodium bicarbonate is gradually added to a slightly sulfuric yellow solution of cerium sulfate, CO_2 is evolved while a white precipitate forms and then disappears in an excess of reagent, giving a yellow liquid. If this liquid is heated, it soon reaches its maximum yellow coloration before losing it completely while a white precipitate then forms.

- Pour a yellow sulfuric aqueous solution of cerium sulfate into a test tube. Then add a few drops of H_2O_2. The liquid becomes completely decolorized. Next add a few drops of ammonia. A brick-red precipitate forms.

Mercury Salts (Mercurous + / Mercuric ++)

- Prepare a solution of mercury nitrate and then add a solution of NaCl. A white precipitate of mercurous chloride is obtained. This substance was formerly used in medicine and was given the name calomel. Next, mix this calomel with a dilute solution of KI. A green mercurous iodide is obtained. A dilute KI solution must be used because if KI is present in excess, mercury itself precipitates.

- Prepare one solution of mercury(II) chloride (8 parts) and another of potassium

iodide (10 parts). When these are mixed, a red precipitate of mercuric iodide is obtained. This precipitate is soluble in ether, benzene, and alcohol. It becomes yellow when heated.

- Pour a solution of HI into a solution of mercury(II) chloride. An orange-red precipitate of mercuric iodide is obtained.

- Dissolve 10 g of mercuric chloride in 200 mL of water. Pour this solution into an aqueous alcoholic KOH solution (60 g of alcoholic potash per liter of water). A yellow precipitate forms and is washed until the wash waters no longer precipitate silver nitrate. Yellow mercury oxide is thus obtained. This oxide disappears in the cold in oxalic acid, forming mercuric oxalate. The same occurs in acetic acid, where it forms mercuric acetate. When brought into contact with an aqueous solution of a ferrous salt, it produces first a green precipitate and then a black one.

- Pour a solution of mercury(II) chloride into a test tube and then add a solution of NaOH. A yellow precipitate immediately forms. It consists of oxide and not hydroxide, the latter being unstable (as in the case of silver hydroxide) and being immediately transformed into oxide. This precipitate settles rapidly. Decant the supernatant liquid, add distilled water, shake, and divide the suspension into two portions.
Into the first portion, pour H_2O_2. The reaction begins slowly and then tends to accelerate. Ultimately, a colorless liquid remains together with a black powder at the bottom.
Into the second test tube, add a little phosphoric acid. The precipitate disappears and the liquid becomes colorless.

- Prepare an aqueous solution of mercury(II) chloride and divide it into two portions. React the first with KOH solution. A yellow precipitate of HgO is obtained, relatively similar to red mercury oxide. If the oxide is dried and then heated, oxygen is released and mercury remains. Care should be taken not to inhale mercury vapors if the substance is heated too strongly or for too long.
Into the second portion of the original solution, bubble H_2S. At first sulfur makes the liquid milky, then distinctly yellow sulfur appears and finally black mercury sulfide forms. If this latter compound is heated, it becomes red, then sulfur is released and mercury remains. Same remark than above.

- Pour NH_4OH into a solution of mercuric chloride. A white precipitate of mercury chloramide forms (which explodes upon contact with Cl_2!). If this precipitate is heated in an excess solution of NaOH, yellow mercuric oxide and NH_3 are formed.

- Into a solution of mercuric chloride, pour a little tin chloride. A pale yellowish-white precipitate first forms and is then transformed into black mercury.

- Into an aqueous solution of mercury(II) chloride, pour an aqueous solution of potassium sulfocyanide. A pale yellowish-white precipitate forms.

- Place a drop of mercury chloride on a copper sheet. At that spot, an amalgam stain forms and disappears as soon as the metal sheet is heated.

- Mercuric nitrate in nitric solution develops a white-yellow coloration in a phenol solution.

- Place two drops of mercury and a little aluminum powder in a test tube. Shake, then pour a solution of mercury(II) chloride over the mixture. If nothing happens, add a little water. Hydrogen will be evolved.

- Into a test tube approximately 4 cm in diameter, pour a layer of formic acid 3 to 4 cm high. Carefully pour about 2 mL of a fairly concentrated solution of mercuric nitrate in water acidified with HNO_3 on top. At first, nothing happens. Several minutes are required before a slight red vapor appears in the tube and the liquid begins to foam while emitting increasing quantities of reddish fumes. While the liquid remains clear at the bottom, it gradually becomes grayish near the top, where the reaction appears strongest. Then, as the gray coloration spreads throughout the liquid and the reddish fumes tend to diminish, a globule of mercury appears at the very bottom of the test tube. Finally, the liquid clears and only the mercury globule remains.
This experiment, which ultimately produces a globule of mercury where at the outset there was only a transparent liquid, is particularly striking from a pedagogical point of view.

- Into an aqueous solution of mercury chloride, pour an aqueous solution of sodium silicate. A pale yellowish-white precipitate is obtained.

- Place a little mercury(II) chloride and sugar in a test tube. Moisten with a little water and add a ball made from aluminum foil. After a short time, the liquid becomes grayish and the reaction accelerates. Ultimately, a small drop of mercury is obtained.

Silver Salts

- Treat a silver nitrate solution with a dilute bromine water solution. A yellow precipitate forms and slowly darkens on exposure to light.

- Using HCl, HBr, HI, and an aqueous solution of oxalic acid, prepare four precipitates by reacting them with an aqueous solution of $AgNO_3$. All of these precipitates dissolve in concentrated NH_4OH.

- Prepare a precipitate of silver chloride by mixing, for example, a solution of silver nitrate with a solution of sodium chloride. As soon as the white precipitate has formed, pour a solution of sodium hyposulfite over it. The precipitate immediately disappears. The same disappearance of the precipitate occurs if a solution of sodium

cyanide is used. If the experiment is repeated using a hot sodium thiosulfate solution, the precipitate is black.

- Mix a solution of KI with a solution of silver nitrate. A milky yellow precipitate of silver iodide forms.

- Into a solution of silver nitrate, pour a solution of sodium hydroxide. A brown precipitate of silver oxide, Ag_2O, forms and not a hydroxide, the latter being unstable and rapidly transforming into the oxide. We have likewise seen page 303, that reacting mercury(II) chloride with sodium hydroxide produces mercury oxide.

- Into an aqueous solution of silver nitrate, pour an aqueous solution of potassium carbonate. A white precipitate of silver carbonate is obtained. Next, dilute with a large quantity of water and heat for a long time. Little by little, silver hydroxide and carbonic acid are formed, the former being rapidly transformed into brown silver oxide (see above), and the latter into water and carbon dioxide.

- Into a solution of potassium dichromate or chromate, pour a solution of $AgNO_3$. A brick-red precipitate is obtained which dissolves in NH_4OH.

- Place dilute phosphoric acid and a few drops of phenolphthalein in an Erlenmeyer flask. Then add dilute ammonia while stirring. When the liquid turns pink, add a very small amount of acid so that it becomes colorless again. Take a small portion of this liquid and add a solution of $AgNO_3$. A yellow precipitate of trisilver phosphate is obtained.

- Into a solution of silver nitrate, pour a solution of HCl and immediately afterward add a piece of zinc. The white precipitate of silver chloride soon disappears through contact with nascent hydrogen, and silver is subsequently recovered in the form of a black powder.

- Into a solution of silver nitrate, slowly pour a solution of an alkaline sulfocyanide. A white precipitate forms but dissolves in an excess of sulfocyanide.

- Into an aqueous solution of silver nitrate, add an aqueous solution of sodium cyanide drop by drop. A white precipitate forms which, after becoming denser, gradually dissolves in an excess of reagent. The reaction is sensitive (requiring only small amounts of salts) and appears almost "magical" from a pedagogical standpoint if carried out, for example, with the aid of a magnetic stirrer slowly mixing the liquid.

- Into a test tube containing water and iron arsenate (which is only slightly soluble), pour silver nitrate. Gradually, the arsenate at the bottom of the test tube acquires a brick-red color. The phenomenon is accelerated by heating.

- Into an aqueous solution of silver nitrate, pour an aqueous solution of sodium sulfite. A white precipitate forms. It is soluble in an excess of sulfite solution and

gradually turns brown in full light.

- Add a small spatula-tip quantity of tin(II) chloride to an aqueous solution of silver nitrate and shake. A mauve flocculent precipitate immediately forms.

Gold Salts

- If, by one means or another, an aqueous solution of gold(III) chloride has been obtained and there is concern that it may be mixed with other chlorides, ether may be added to the solution and the mixture shaken vigorously. Since gold(III) chloride is even more soluble in ether than in water, it will pass into the ether layer. It then suffices to decant and allow rapid evaporation in order to obtain crystals of the salt.

- Place in a test tube an aqueous solution of gold chloride obtained by bubbling Cl_2 through water containing a sheet of gold. Then pour over it an aqueous solution of arsenious oxide as concentrated as possible and shake thoroughly. Allow the mixture to stand for at least 24 hours. A thin layer of gold is thus deposited on the walls of the test tube.

- Into a solution of gold chloride (or chloroauric acid), pour a solution of an alkaline bromide or hydrobromic acid. The liquid changes from yellow to orange and then to deep red as more reagent is added.

- Into an aqueous hydrochloric solution of gold chloride, pour an aqueous solution of sodium nitrite. Gradually, the color changes from yellow to bluish-green owing to the appearance of a fine dark precipitate of gold which eventually settles.

- Begin by preparing a solution of gold tribromide by digesting a piece of gold leaf in bromine water and then heating to expel the excess bromine. Pour a little of this tribromide solution into a very small amount of aqueous NaOH solution and then add to this mixture a few drops of hydrogen peroxide. A navy-blue color, almost black, appears.
This same color also appears if a few drops of the solution are placed on sucrose, a paracetamol tablet, crystals of phenol, or vitamin C (from left to right in Figure 130).

Figure 130

- Dissolve a small spatula-tip quantity of stannous chloride in water acidified with HCl. Then add a few drops of a solution of gold chloride. A mauve coloration rapidly develops, resulting from an extremely fine precipitate which eventually settles. It is useful to know that, in very thin layers, gold does not appear yellow but purple when seen by transmitted light.

- Into a hydrochloric solution of gold chloride obtained by means of aqua regia, pour a little sulfurous acid. Within about one minute, the liquid becomes brown and a golden film appears on the surface. After settling, a brown powder of gold is deposited at the bottom. The addition of a little nitric acid is sufficient to make this powder disappear, and the liquid regains all of its transparency together with its original greenish-yellow color. With a solution of gold chloride obtained by bubbling chlorine through water containing a sheet of gold, the reaction is slower and the gold is often deposited on the walls of the test tube as a very thin coating which appears red from certain angles, the liquid itself then sometimes appearing very slightly blue. This experiment shows the unusual colors that gold may exhibit when deposited as an extremely thin layer.

Manganese Salts, Manganates, and Potassium Permanganate

- When hydrobromic acid is poured onto manganese dioxide, a brief sound is heard and the reaction then continues very slowly. It can be accelerated by gentle heating. Once decanted, the liquid takes on a greenish-yellow color.

- Dissolve a small amount of manganese chloride in ethyl alcohol and ignite it. Instead of remaining blue, the flame becomes red.

- An aqueous solution of manganese chloride does not keep well because part of it is gradually transformed into manganese dioxide. Light also acts rather rapidly on the same solution by causing a more rapid precipitation of manganese dioxide. Other substances produce the same effect. Thus, for example, if a little potassium chromate solution is added to a solution of manganese chloride, the same precipitation occurs within about half an hour. A strip of magnesium ribbon placed in a solution of manganese chloride becomes brownish-pink after a day as the metal is precipitated.

- Add a little NaOH to a solution of manganese chloride. An insoluble precipitate forms that does not dissolve in an excess of sodium hydroxide. This precipitate turns brown on exposure to air. The oxidation can be accelerated by bromine water. In that case, the precipitate, which was originally gelatinous, becomes black and powdery. Manganese dioxide has been formed.
The same occurs when chlorine water is used instead of bromine water.
This reaction was formerly used to dye cotton brown. Here is how it may be verified. Take a piece of perfectly white cotton and soak it in a solution of manganese chloride. Remove it with a fine pair of forceps and immediately immerse it in a solution of sodium hydroxide. Remove it after two or three seconds and rinse it. All

that remains is to allow it to dry.

- Add a little ammonia to a solution of manganese chloride. A white precipitate forms, sometimes with a yellowish tint. If ammonium chloride has first been added, no precipitate appears.

- To an aqueous solution of manganese chloride containing glycerine, add a little sodium hypobromite. A brown precipitate is obtained. Had the glycerine not been added, a blackish precipitate of metamanganic acid would have been obtained. When this latter precipitate is heated, its color tends increasingly toward brown and then red (formation of permanganate), especially if a little copper sulfate has been added before heating.

- Add a little sodium hypochlorite to a solution of manganese chloride. A brown precipitate of manganese dioxide forms immediately.

- Add ammonium sulfide to a solution of manganese chloride. A salmon-colored precipitate appears. If an excess of ammonium sulfide and a little ammonia are added and the mixture is heated, the precipitate gradually turns green.

- Add a solution of potassium ferrocyanide to a solution of manganese chloride. A white precipitate is obtained.

- Place a small amount of manganese carbonate in contact with HCl. The liquid effervesces and then, when diluted with water, yields a transparent pinkish solution of manganese chloride.

- Add an aqueous solution of sodium silicate to an aqueous solution of manganese sulfate. A white precipitate is formed.

- Take a thoroughly clean bottle and pour into it an aqueous solution of potassium chromate, then carefully add an aqueous solution of manganese sulfate on top. Very quickly, the solution turns very dark brown and then, more slowly, a layer of basic manganese chromate adheres to the glass walls of the bottle. If the solutions are too dilute, the liquid turns light brown and only a slight deposit forms and settles at the bottom of the vessel.

- A solution of manganese chloride poured into a solution of potassium permanganate produces a precipitate of manganese dioxide, causing the solution to become dark brown. The flocculent precipitate settles slowly. It can be verified that the liquid has become acidic owing to the formation of Hcl.

- To a rather dilute solution of potassium permanganate, add two or three drops of NaOH solution and then some ethyl alcohol. The green color of the manganate ion immediately appears.

- If KOH or NaOH is added to an aqueous solution of permanganate together with a little filter paper (or even large flakes of dust), and the mixture is shaken vigorously, the solution gradually becomes green at room temperature. Without filter paper or dust, the mixture must be heated before it turns green through formation of the manganate ion.

THE MINERAL CHAMELEON

Because of the ease with which the pink-purple-violet permanganate ion (depending on the concentration of the salt in solution) is transformed into the green manganate ion, potassium permanganate was formerly nicknamed the "mineral chameleon."

- Prepare a pink solution of permanganate containing a little NaOH. Pour cyclohexane on top and shake vigorously, preferably using a mechanical shaker. The solution rapidly becomes green through formation of manganate.

To a solution of permanganate made alkaline with NaOH, add a solution of sodium hyposulfite. The liquid immediately turns green. If the permanganate solution is dilute and left neutral, the addition of hyposulfite turns it brown.

Dissolve 3 g of NaOH and 4.5 g of sugar in 250 mL of water. Place the flask containing this solution on a magnetic stirrer and pour a purple solution of potassium permanganate into the center. Very quickly, the purple color changes to blue, then to emerald green, then to pale green, and finally turns Naples yellow (Figure 131).

Figure 131

- A solution of potassium permanganate is immediately decolorized when a solution of ferrous sulfate is added.
This very simple experiment may be made more elaborate by preparing the ferrous sulfate oneself from iron oxalate. To do this, boil a solution of sodium hydroxide and pour powdered iron oxalate into it. A greenish-white precipitate of iron(II) hydroxide is formed. Allow it to settle rapidly and pour off as much of the supernatant liquid as possible. Add boiled water, allow it to settle again, and remove

as much of this water as possible, thus washing the precipitate more or less adequately. Convert this precipitate into a solution of ferrous sulfate by adding H_2SO_4 drop by drop until the liquid becomes clear. Caution: each drop produces a vigorous reaction accompanied by splashing. It is therefore preferable to work in a vessel with high walls and a narrow neck, such as a test tube or an Erlenmeyer flask. Finally, add a solution of potassium permanganate. It will immediately lose its color.

- Arrange five test tubes side by side. Leave the first empty. Into the second place one drop of H_2SO_4. Into the third add a few drops of a NaOH solution, into the fourth a few drops of a KOH solution, and into the last a few drops of a dilute NH_4OH solution. Next prepare a moderately dilute aqueous solution of sodium sulfite. Finally, prepare a purple solution of potassium permanganate that is not too opaque. Pour the permanganate solution into each test tube to a depth of about 4 centimeters. Then add a little of the sulfite solution to each tube. In the first test tube, the liquid immediately changes from purple to a raw sienna yellow while remaining apparently clear. It will, however, later be observed that small brick-red particles gradually form and eventually settle. The liquid in the second test tube is decolorized very rapidly and then remains unchanged. The liquid in the third test tube immediately turns green, then blue, then yellow as more sulfite solution is added. Although the liquid initially remains clear, it later becomes more or less cloudy and finally deposits a reddish precipitate. The same occurs in the other two test tubes, although with subtle differences. In the first of these, a precipitate of MnO_2 is formed. In the second, colorless sulfates are produced. In the three preceding test tubes, the reaction is much more complex and therefore varies according to concentration and time. A manganese salt of the type Na_2MnO_4 is first formed. This reacts with water to regenerate hydroxide and permanganate, ultimately leading to the formation of MnO_2.

- A solution of permanganate acidified with a little H_2SO_4 is immediately decolorized by sulfurous acid in solution as well as by gaseous SO_2 (the "wine turned into water" experiment described earlier).

- A solution of potassium permanganate is decolorized at room temperature by a solution of ascorbic acid or citric acid. Vigorous mixing may be necessary.

- A solution of permanganate acidified with H_2SO_4 is decolorized by the addition of a sodium nitrite solution.

- Prepare a moderately dilute aqueous solution of potassium permanganate in a test tube, then add a lancet-tip quantity of tin(II) chloride. Shake. Decolorization occurs immediately.

- Mix a solution of potassium permanganate with a solution of arsenious oxide. Slow decolorization takes place. The reaction is faster if the permanganate has first been acidified with H_2SO_4.

- Place in a flask an aqueous solution of potassium permanganate concentrated enough that one cannot see through it. Acidify it rather strongly with concentrated H_2SO_4. Then add lactic acid to the mixture. Foam appears and the mixture warms up. The liquid changes from violet to brown, then yellow, and finally colorless, while a pungent odor, very similar to that of formaldehyde, becomes noticeable. Among other products, acetaldehyde or ethanal has been formed. The reaction proceeds more rapidly if the mixture is gently heated. It also works, though less vigorously, if the permanganate is not acidified beforehand, since lactic acid itself acts as an acidifying agent.

- Pour a dilute solution of H_2SO_4 into a test tube and add a tiny crystal of potassium permanganate, just enough to color the liquid. Then add a piece of zinc. The solution gradually becomes colorless.

- Prepare a 50:50 mixture of H_2SO_4 with a concentrated solution of oxalic acid. Allow it to flow drop by drop (from a stopcock burette) into an acidified solution of potassium permanganate placed in a tall vessel standing on a magnetic stirrer running continuously. Colorless manganese sulfate is gradually formed, the solution passing from violet to brown, then yellow, and finally clear. Depending on the concentrations, however, the change may occur quite abruptly.

- A somewhat more concentrated than usual solution of permanganate, acidified with H_2SO_4, is poured into a large flask placed on a magnetic stirrer. The flask is connected on one side to a funnel through which a concentrated solution of phenol in water is allowed to flow slowly and, on the other side, by a delivery tube, to a wash bottle containing limewater. In the flask, the permanganate is gradually decolorized while formic acid and oxalic acid are formed (the latter recognizable by the precipitate it gives with a solution of $CaCl_2$). The limewater, meanwhile, becomes cloudy.

- Add a drop of glycerine to an alkaline solution of permanganate and shake. The liquid changes from purple to green and then to red. If a solution of $CaCl_2$ is then added, a white precipitate of calcium oxalate forms. Owing to the color of the liquid, this precipitate may appear pink before it has settled.

- Prepare a weakly concentrated solution of $KMnO_4$ in a large test tube and add a pinch of sodium perborate. Oxygen is evolved and a precipitate of MnO_2 is formed. (See the chapter dealing with the preparation of oxygen in the laboratory.)

- Prepare a solution of potassium permanganate that is not too concentrated, but concentrated enough that it is no longer transparent. Half-fill another flask with water and dissolve some sodium hydrosulfite in it by shaking. Then gradually pour the permanganate solution into this latter flask while stirring. At first, the permanganate is decolorized, but little by little a brownish-black flocculent precipitate forms and steadily increases in both quantity and density. Allow the mixture to stand. The precipitate settles to the bottom of the flask. It is manganese

dioxide.

- Add a few drops of formic acid to a solution of Na_2CO_3 in order to obtain an alkaline formate. Stir gently. Gas is evolved. Then allow a dilute solution of $KMnO_4$ to flow into it drop by drop. At first, the permanganate is decolorized, but gradually the solution turns yellow and finally brown. Then add the permanganate solution more rapidly until the liquid becomes very dark brown and allow it to stand, or centrifuge it, in order to observe the black deposit.

- Add a little H_2SO_4 to formic acid and then allow potassium permanganate solution to flow into it drop by drop. After decolorization, the solution becomes pink again and the permanganate is no longer affected.

- Prepare two solutions of permanganate. Add a little H_2SO_4 to one and a little NaOH to the other. Then add formic acid to both. The colors obtained are markedly different.

Figure 132

- Place powdered oxalic acid in a flask and add powdered potassium permanganate on top of it. Shake rapidly to mix them roughly. Sometimes, when the oxalic acid is moist and the mixing has been sufficiently vigorous, the reaction starts by itself. Otherwise, a drop of water must be added. Once initiated, the reaction is relatively vigorous and distinctly exothermic, yet not at all dangerous. Large amounts of water vapor and carbon dioxide are evolved, the latter being easily identified by bubbling it through limewater or baryta water (Figure 132). If more water is added, the reaction starts again. At the end, and after cooling, manganese dioxide is found coating the walls of the flask. It can easily be removed with a little hydrogen peroxide.
The same experiment may be performed in a slightly different manner by first reducing the permanganate and the acid separately to powders and then placing them, thoroughly mixed, in the form of a narrow strip on a refractory stone or a porcelain dish. A drop of water placed at one end of the strip usually initiates a reaction that propagates from one end to the other with a hissing sound and the evolution of gas.
The same reaction in aqueous solution is quite different. Indeed, if a solution of oxalic acid is poured into a solution of potassium permanganate, slow decolorization takes place and is accelerated only by gentle heating.

- Place a neutral solution of potassium permanganate in a flask. Then add methyl alcohol. Even at room temperature, a change in color is observed fairly rapidly and continues during the following hours until the liquid becomes brown while nevertheless remaining transparent. This transformation takes place within about a minute if the liquid is brought to a boil. After a certain number of hours, a

brownish-red flocculent precipitate appears.

- Pour a solution of potassium permanganate into a beaker containing milk. The color gradually changes and finally becomes brown owing to the deposition of manganese dioxide. If, instead of a permanganate solution, a generous quantity of permanganate crystals is poured into the beaker, the liquid begins to foam and the transformation into "artificial charcoal" is immediate.

Chromium Salts, Chromates, and Dichromates

CARCINOGENIC SUBSTANCES

Chromium salts are now regarded as highly carcinogenic and, for this reason, their circulation (like that of other substances presenting the same hazards) is now restricted. It is strongly recommended to wear latex gloves when handling them, since poisoning can occur through the skin. This seems an appropriate moment to remind the reader once again that chemistry is not a science without dangers and that it should be practiced while observing a whole series of safety rules. One must be just as careful when transferring certain fine powders as when working with gases that must under no circumstances be inhaled.

- Place a small amount of chromic anhydride (chromium(VI) oxyde) in a small dish. Using a pipette, allow drops of sodium bisulfite to fall onto it. The substance is immediately transformed into a green oxide. The reaction is fairly vigorous. Keep at a distance.

- Place a small amount of powdered chromic anhydride in a porcelain crucible. Allow a few drops of benzene to fall onto it. The anhydride gradually turns black.

- To a yellow solution of chromic anhydride (which in reality contains a mixture of chromic acid H_2CrO_4 and bichromic acid $H_2Cr_2O_7$), gradually add H_2SO_4. As each drop falls, the solution becomes redder because the equilibrium is displaced and increasing amounts of bichromic acid are formed.

- Pour 1 cm of 33% hydrogen peroxide into a test tube and add an equal quantity of water in order to dilute it. Then add a tiny fragment of chromic anhydride. The reaction is vigorous. At first, a blue liquid is seen to form, but it rapidly turns brown. Add ether and shake. The upper layer becomes blue-violet owing to the formation of perchromic acid.
Here is another way of performing this experiment. Take an Erlenmeyer flask (rather than a flask or a beaker) and pour into it a dilute solution of chromic acid. The color should be yellow, like urine. In another vessel, prepare some 33% hydrogen peroxide diluted with an equal volume of water and fill a dropper pipette

with it. Place the stirrer bar in the Erlenmeyer flask, add ether, and set the magnetic stirrer to a high speed. Immediately begin adding the hydrogen peroxide drop by drop. The liquid becomes deep blue. Stop the stirring and immediately pour the contents into a separatory funnel, which is then closed with its ground-glass stopper. Two liquids separate, the upper one being blue because it consists of perchromic acid dissolved in ether. The blue color gradually fades and disappears completely within about ten hours.

- Add an aqueous solution of sodium or potassium carbonate to an orange solution of chromic anhydride. Carbon dioxide is evolved and the liquid turns yellow (chromate ion).

- Place a small amount of chromium(VI) oxide in absolute ethyl alcohol. The liquid becomes slightly colored and, after a few hours, a black solid is deposited. Pour off the alcohol, recover a few particles of this black substance, and heat them with a few drops of HCl. The liquid develops a beautiful emerald-green color. A particular chromium oxide had in fact been formed, which reacts with the acid to produce a chloride. Had the chromium(VI) oxide been treated directly with hot HCl, red fumes of chromyl chloride would have been evolved.

Pour an excess of concentrated hydrochloric acid onto CrO3 (chromic anhydride). The reaction is slow and the odor of chlorine can be detected. Although the liquid is initially brownish-red, it ultimately becomes dark green, or emerald green when diluted with water. It is a hydrochloric solution of chromium chloride.

Dissolve chromic anhydride in hydrochloric acid and, without waiting, add sulfuric acid drop by drop. Highly toxic chromyl chloride is evolved as red fumes (see Chapter 15.7 for further information on this compound).

- Place a little green chromium oxide into four test tubes. Then allow it to react respectively with HCl, HNO_3, H_2SO_4 , and aqua regia. After twenty-four hours or a longer period, the liquid in the test tube containing HCl becomes yellow. After reaction and standing, the aqua regia appears yellowish-red. Nothing happens in the other two test tubes.

- Add a solution of potassium or sodium nitrite to an aqueous solution of chromic anhydride to which a little HCl has been added. The solution immediately turns green through the formation of a chromate.

- Add an aqueous solution of an alkaline sulfide or polysulfide to an orange solution of chromic anhydride. A dirty yellow-green or yellow precipitate is formed.

- Add H_2O_2 to an orange aqueous solution of chromic anhydride. The liquid immediately becomes very dark brown-black and foams strongly. When the reaction has subsided, add a solution of ammonia and heat, adding a little more H_2O_2 if necessary. The liquid becomes lemon yellow, indicating the appearance of the

chromate ion.
The experiment may also be performed differently. Ammonia may be added directly to the initial chromic anhydride solution. The solution then immediately becomes lemon yellow. If H_2O_2 is subsequently added, the liquid turns a transparent brownish-red. If this liquid is heated, oxygen is evolved vigorously and the entire solution returns to its original lemon-yellow color.

CHROMIUM SULFATE

Depending on its method of preparation, chromium sulfate may be either green or blue-violet in color. It then gives green or blue solutions.

- Prepare an aqueous solution of green chromium sulfate without taking any special precautions. Gradually, over a period of days, it will change color and become blue.

- A solution of chromium(III) sulfate gives, with a solution of potassium phosphate, a precipitate of green chromium phosphate which eventually disappears, yielding a beautiful green liquid.

- Add ammonia to a bluish solution of chromium sulfate. A slight greenish precipitate forms and gradually turns blue-gray. If enough ammonia has been added, the precipitate appears pink when viewed by transmitted light. The reaction is more obvious if the chromic salt solution has first been heated.
The same experiment may be performed with a green solution of chromium chloride.

- Add an aqueous solution of sodium silicate to a bluish aqueous solution of chromium(III) sulfate. A grayish-green precipitate is obtained.

- Add a little hydrogen peroxide to a green solution of chromium(III) sulfate. The solution slowly turns a dirty yellow.

- Add a solution of ammonium sulfide to a solution of chromium(III) sulfate or chromium(III) chloride. Chromium hydroxide is formed because the sulfide is unstable in the presence of water.

- Prepare eight test tubes. Into the first four, pour a green solution of chromium(III) sulfate. Into the remaining four, pour a violet-blue solution of chromium(III) sulfate. Then react each group respectively with a solution of potassium carbonate, a solution of ammonium sulfide, a solution of sodium hydroxide, and dilute ammonia. The reactions in the tubes containing the green chromium sulfate solution are relatively weak, except with ammonium sulfide. In contrast, the reactions in the tubes containing the violet salt solution are rapid and clearly visible in every case, being marked by significant color changes or the formation of precipitates.

- If a drop of H_2O_2 is added to a solution of potassium chromate, the liquid immediately becomes brownish-red with green reflections and then begins to foam. The original yellow color gradually reappears as the foaming ceases.

- Into a series of test tubes, pour respectively aqueous solutions of ferrous sulfate, ferric chloride, zinc sulfate, cobalt(II) chloride, copper(II) sulfate, nickel sulfate, and manganese(II) chloride. Then, without excessive stirring, add a little aqueous potassium chromate solution to each test tube. Depending on the case, either clear colored solutions or colored precipitates of various appearances are obtained (Figure 133).

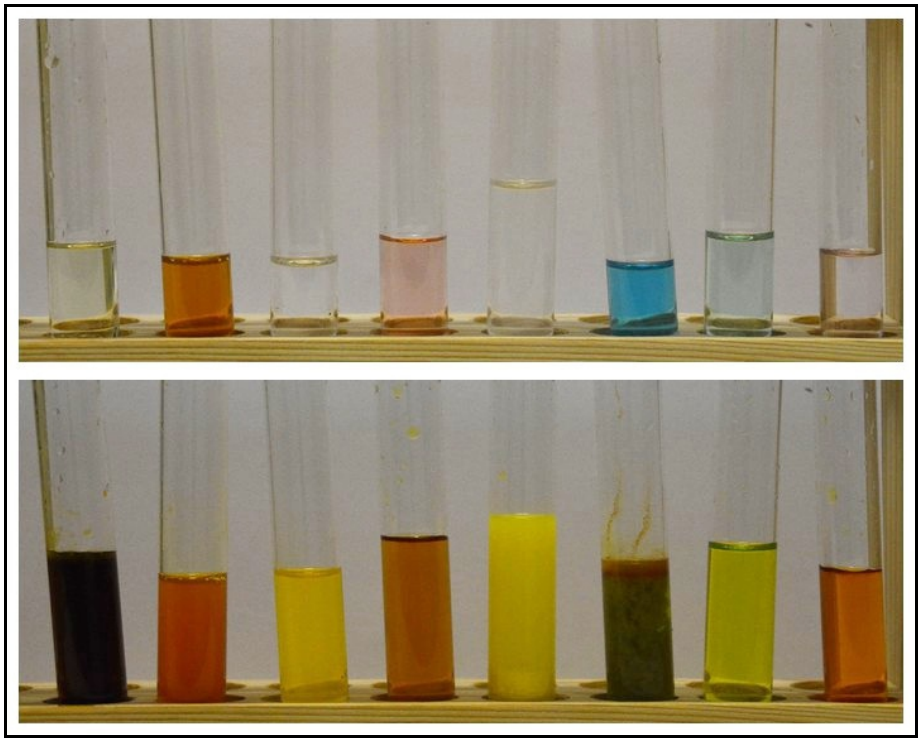


Figure 133

- A solution of potassium chromate added to a solution of lead acetate gives a yellow precipitate of lead chromate. A clear liquid of the same color is obtained if a little HCl is poured on top.
If the potassium chromate solution is first made slightly alkaline, an orange-yellow precipitate of basic lead chromate is obtained instead of the yellow precipitate of lead chromate. If a solution of NaOH is then added progressively, the entire precipitate disappears and the liquid becomes canary yellow.

- If a colorless solution of barium chloride is added to a yellow solution of potassium chromate, a lemon-yellow precipitate is obtained that is used in painting. If HCl is then added, the precipitate disappears while the now clear solution becomes more orange owing to the formation of a dichromate. A solution of dichromate, on the other hand, gives with barium chloride a tangerine-yellow precipitate that forms slowly and adheres here and there to the walls of the flask.

- If a solution of potassium chromate is poured into baryta water, a rather compact lemon-yellow precipitate of barium chromate forms and then, after stirring, settles slowly.

- A solution of strontium chloride mixed with a solution of potassium chromate produces a very fine lemon-yellow precipitate that takes a long time to settle.

- If a little sugar (sucrose) and then two drops of sulfuric acid are added to a solution of potassium chromate, a dark orange coloration appears rather quickly and, upon heating, changes to a dirty green. The sugar may be replaced by ethyl alcohol.

- Add a solution of citric acid to a solution of potassium chromate. The color changes to orange owing to the formation of a dichromate.

- Place a fairly dilute solution of potassium chromate in a large test tube. Add two or three drops of H_2SO_4. Then add an equal or smaller volume of alcohol and shake. Finally, allow concentrated H_2SO_4 to run down the side of the test tube. A blue solution immediately forms and sinks to the bottom of the tube. This is the principle behind the traditional police breathalyzer. The odor subsequently released from the tube is pleasant but irritating to the eyes.

- A solution of potassium chromate gives a brick-red precipitate with a solution of silver nitrate, whereas a dichromate solution gives a slightly darker precipitate.

- Prepare a solution of an alkaline dichromate and then dilute it heavily. The color gradually changes from orange toward yellow owing to the formation of chromate.

- Add a solution of NaOH or KOH to a not overly concentrated solution of potassium dichromate ($K_2Cr_2O_7$). The orange color immediately changes to the same yellow as picric acid owing to the formation of chromate.
If a very concentrated dichromate solution is used, however, a beautiful emerald-green coloration is obtained. Conversely, if the alkaline solution is replaced by an acidic solution (for example concentrated HCl), the solution becomes redder owing to the formation of dichromate.

- Into a light-orange solution of potassium dichromate filling about three-quarters of a test tube, add a few drops of concentrated H_2SO_4. After shaking, introduce a strip of zinc. Hydrogen is evolved and the color of the liquid rapidly changes to a dirty brown, then within about an hour to green, and finally to duck-egg blue. This color, however, is visible only when the test tube is placed in front of a strong light source; otherwise the solution appears ink-black. This experiment succeeds only with a sufficiently dilute dichromate solution and with enough acid and metal to maintain a prolonged evolution of hydrogen. If no gas is evolved, the solution merely darkens slowly while passing through a brown coloration. Another precaution must be observed: the experiment must be carried out away from air. Indeed, if the chromic solution (corresponding to Cr_2O_3) is transformed into a chromous solution, the blue

chromous salts corresponding to CrO are rapidly oxidized by air and become green. The same experiment may be performed with iron instead of zinc.
Here is a variation. Into an Erlenmeyer flask place 25 g of zinc, 75 mL of concentrated HCl, 50 mL of water, and 4.25 g of potassium dichromate. The reaction is vigorous and continues as long as zinc remains. The liquid gradually changes from green to blue. Withdraw a portion of it and add a 10% solution of sodium acetate. A red precipitate of chromium(II) acetate is formed or, at the very least, a distinct color change is observed. If concentrated HCl were added to the precipitate after decantation, a chromium chloride solution would be obtained that turns green on exposure to air.

- Add an aqueous solution of arsenious oxide (which is only sparingly soluble) to an aqueous solution of potassium dichromate. One must wait twenty-four hours before observing a precipitate settling to the bottom of the test tube.

- Add potassium carbonate progressively to a solution of potassium dichromate. The solution changes from orange to yellow owing to the formation of potassium chromate.

- Add a solution of barium chloride to a solution of potassium dichromate. At first nothing happens, then the liquid becomes cloudy and finally a precipitate appears, giving the liquid an orange tint. Once settled and after the liquid has been removed, this precipitate appears yellow.

- Add a freshly prepared solution of sodium sulfite to an orange solution of potassium dichromate. The color changes immediately. No change occurs, however, if the same sodium sulfite solution is added to an aqueous solution of potassium chromate. Nevertheless, even after a long time has elapsed, if a little HCl is poured into this flask, the color immediately changes from yellow to duck-egg blue.

- Add a little ferrous sulfate solution to an orange solution of potassium dichromate. The color immediately changes, passing through brown. The same experiment carried out with potassium chromate produces a light-brown precipitate.

- Add a freshly prepared solution of sulfurous acid to a dilute solution of potassium dichromate. The color immediately changes to green or blue, depending on the concentration. Chromium sulfate is formed.

Pour a solution of potassium dichromate into a long test tube to a depth of about 3 to 4 cm. Acidify it with one or two drops of H_2SO_4. Then add 7 to 8 cm of ether. The two liquids remain superimposed without mixing. Finally, using a pipette, allow two drops of H_2O_2 to run down the wall of the test tube. When these drops reach the surface of the dichromate solution, a deep-blue cloud forms. This cloud gradually fills the colored portion of the dichromate solution while, above it, the ether slowly turns blue and bubbles rise to the surface. Ultimately, if nothing further is done, the lower part of the tube becomes a very dark blue, almost black and opaque, while the

upper part turns a translucent blue (Figure 134). If additional drops of H_2SO_4 and H_2O_2 are then added, the upper layer eventually becomes colorless while the lower layer turns very dark green. In this reaction, the colors of the various constituents may vary considerably according to concentrations and reagent quantities.

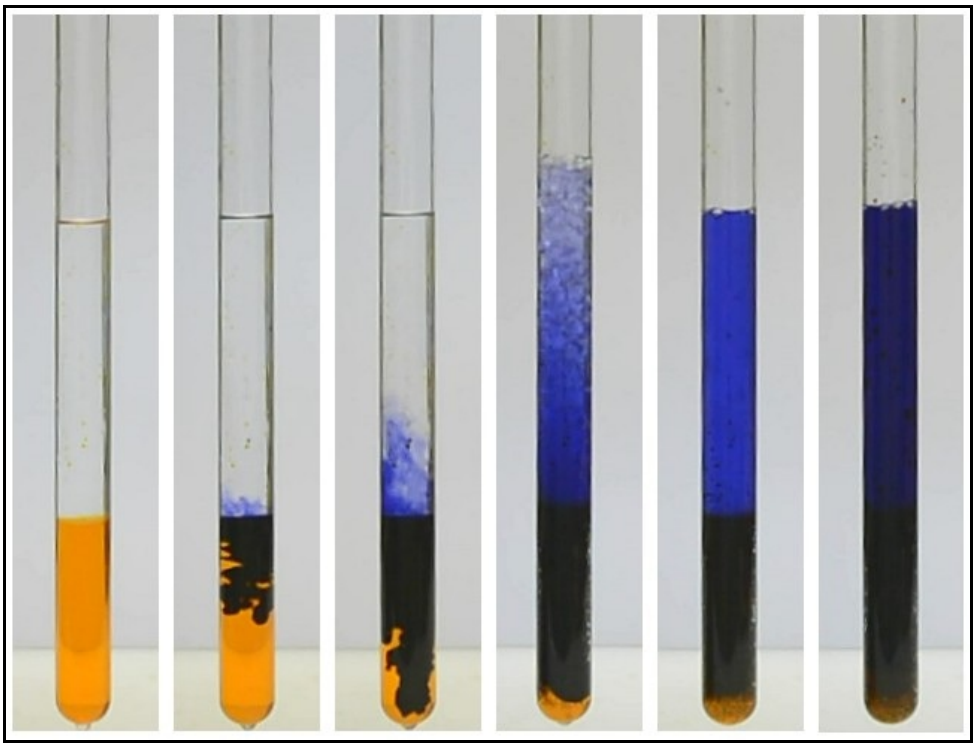


Figure 134

Here is a slightly different way of performing this experiment. Prepare a light-orange solution of potassium dichromate (not too concentrated) and pour it into a test tube. Then add 1 cm of ether, which will float on top. Next, add diluted H_2O_2. The liquid becomes black and oxygen is evolved. The ether gradually turns blue, although this color remains short-lived. If, instead of H_2SO_4, NaOH is added at the beginning, a red coloration is obtained, either transient or permanent depending on the concentrations.

Here is another variation of this experiment. Fill a 250 mL tall-form beaker to about nine-tenths of its height with a 1% aqueous solution of H_2SO_4. Add four or five drops of H_2O_2 and stir so as to create a gentle swirling motion. Finally, sprinkle in crystals of potassium dichromate (or sodium dichromate). The crystals rapidly fall to the bottom while leaving behind blue-to-violet colored filaments. If the mixture is then stirred vigorously, a beautiful blue liquid is obtained, which gradually becomes lighter, passing through a pale green coloration. This experiment gives the same results with potassium chromate (or sodium chromate).

REMARK: The blue color observed here is produced by per(oxy)chromic acid, which allows very small quantities of hydrogen peroxide to be detected.

- A mixture of water, $K_2Cr_2O_7$, and H_2SO_4 is poured into a test tube. Isopropyl alcohol is then added on top. The tube warms up, bubbles are evolved, and boiling may even

occur. This is followed by a sudden separation into a very black liquid and a beautifully blue liquid.

- In a mixture of hydrogen peroxide and NaOH, potassium dichromate in solution produces a red liquid from which oxygen is soon evolved.

- In a 250 mL Erlenmeyer flask, place equal parts of sawdust and potassium dichromate, just enough to cover the bottom with a layer 2 to 3 mm thick. Connect the flask to a Drechsel bottle containing baryta water and, through a safety funnel, allow sulfuric acid to flow in gradually. During the first few seconds, very little happens apart from the blackening of the mixture. Then, suddenly, a large quantity of CO_2 is evolved, producing a precipitate in the baryta water. The reaction is highly exothermic. At the end, a green liquid remains which becomes yellow (chromate) when diluted with water.

- Add a little potassium dichromate solution to a solution of bismuth nitrate, which can easily be prepared by reacting bismuth with nitric acid. A dark-yellow precipitate is obtained.

- An alkaline dichromate solution gives, with ammonium sulfide, a greenish-gray liquid.

- An alkaline dichromate solution to which a solution of silver nitrate is added gives a reddish-brown precipitate soluble in HNO_3 or NH_4OH, yielding, in the first case, an orange solution and, in the second, a yellow solution.

- Add isopropyl alcohol to an aqueous solution of potassium dichromate and shake. A white precipitate forms and settles to the bottom of the test tube.

- Into a mixture of potassium dichromate solution and H_2SO_4, add a few drops of aniline. Oily droplets form together with a black-blue-green precipitate.

- Into a flask or a 200 to 250 mL Erlenmeyer flask, place a spoonful of oxalic acid, a little water, and a solution of potassium dichromate. It is observed that the liquid becomes increasingly dark in color, then begins to foam, and that the gas evolved, when passed through a Drechsel bottle containing baryta water, produces a precipitate.

- In a 500 mL pear-shaped flask, place equal weights of tartaric acid and sodium dichromate, taking care not to exceed one-third of the vessel's height. Then add enough water so that the liquid level rises only slightly above the level originally occupied by the two salts. Stir gently with a thin glass rod to facilitate dissolution. Little by little, gas begins to evolve and the reaction then rapidly increases in intensity and runs away, which is why a pear-shaped flask is preferable. The temperature rises very rapidly. When the gas evolved is passed through limewater, a heavy precipitate is observed. The reaction then subsides, leaving a dark-green

liquid containing formic acid, whose odor is perfectly recognizable.

- Add a solution of potassium dichromate to a solution of tannic acid. A brownish-green precipitate slowly forms and settles to the bottom of the test tube.

- Using either a mechanical or magnetic stirrer and an Erlenmeyer flask placed in an ice-water bath, dissolve 50 g of potassium dichromate in 330 mL of water. Once the salt has completely dissolved, gradually add 85 g of concentrated sulfuric acid while stirring vigorously. The temperature rises considerably and stirring is useful in preventing the liquid from boiling. When this operation has been completed, allow the orange liquid to cool, then place the flask in a fresh ice bath and very gradually add 20 g of absolute ethyl alcohol, taking care that the temperature does not rise above about ten degrees Celsius. Allow the necessary time for crystallization while placing a broadly perforated cover over the flask (to minimize the fall of dust while still allowing evaporation). It may be useful to divide the liquid among several crystallizing dishes in order to accelerate crystallization. As early as the second day, beautiful violet-purple crystals of chrome alum may already appear.
If, when the alcohol is added, it is poured in all at once, the color of the liquid suddenly changes to dark green and the temperature rises sharply again, to the point that the entire liquid may begin to boil while giving off toxic vapors. The color will then continue to evolve gradually toward an ink-blue shade. In this case, it is sometimes necessary to seed the solution with an existing crystal in order to induce crystallization.

- Prepare a blue aqueous solution of chrome alum. Slowly add an aqueous solution of NaOH. A precipitate forms and then dissolves in an excess of reagent to give a green liquid. If a solution of ammonia is used instead of NaOH, a precipitate also forms, but this time it does not immediately dissolve in excess reagent. It does, however, dissolve after about an hour, yielding a beautifully mauve solution. Repeat the experiment a third time, using a solution of sodium carbonate. Once again, a precipitate insoluble in excess reagent is formed, but this time it is gray-blue-green in color.

- Add a little chloroform to a sulfochromic mixture, also called sulfochromic acid (potassium dichromate + H_2SO_4), and shake. The color changes from red to brown.

- To a solution of sulfochromic acid diluted until it becomes orange, add a few drops of ethyl alcohol. The solution does not change color immediately, but within about eight hours it turns a deep blue.

In the pages that follow, we will be dealing with metallic salts that, unfortunately, are all too rarely discussed in chemistry books intended for beginners. This is a pity, because they are truly worth examining in some detail.

Vanadium Salts and Vanadates

Vanadium salts, and especially vanadium pentoxide (V_2O_5), occupy a special place in demonstrational chemistry because the color of their solutions changes according to the valence state of the metal, which may be divalent, trivalent, tetravalent, or pentavalent.
For convenience, here is a reminder:
Vanadium dioxide VO or V_2O_2 is violet (V+2)
Vanadium trioxide V_2O_3 is green (V+3)
Vanadium tetroxide V_2O_4 is blue (V+4)
Vanadium pentoxide V_2O_5 is yellow (V+5)

Furthermore, in certain cases, mixtures are formed in which several valence states are present simultaneously. As a result, such salts can produce yellow, orange, red, brown, green, blue, violet, and various intermediate shades, as well as colorless solutions. Vanadium therefore deserves far more than potassium permanganate to be called the "mineral chameleon"!

- Into a test tube, pour four or five centimeters of 33% hydrogen peroxide. Then add a small spatula tip of vanadium pentoxide. The liquid begins to foam and gradually acquires a canary-yellow color. Leave it standing overnight. The liquid (which is still foaming) is then divided into two portions. To the first portion, add a few drops of NaOH solution. The liquid becomes mauve-lilac but slowly fades within one or two hours. To the second portion, add two drops of HNO_3. The liquid becomes ruby red and then slowly turns orange within one or two hours. The first test tube is then brought to a boil. The colorless liquid becomes yellow again. The second tube is heated in the same manner. The red-orange liquid becomes a delicate blue-green.
Variant of the preceding experiment: place about two good centimeters of hydrogen peroxide in each of three large test tubes. Add a few drops of HCl to the second tube and a few drops of NaOH solution to the third. Finally, add a small spatula tip of vanadium pentoxide to each tube. The liquids foam strongly. The tubes containing acid or alkali may, at some point, foam excessively and even overflow. In the first tube, the final result is a yellow liquid that continues to evolve gas for a long time and retains its color even when heated, although the shade may become slightly darker. The acidified tube eventually yields a brownish-yellow liquid that turns green upon heating. The tube containing caustic soda yields a yellow liquid. It becomes red when sulfuric acid is added and then blue-green when heated. The colors obtained vary according to the amounts of acid, base, and vanadium pentoxide used, but also according to temperature.

- Prepare a concentrated solution of vanadium pentoxide in hydrochloric acid of at least 30%. Some authors recommend gently warming the acid, but this does not seem advisable to me because heat may reduce its concentration. It is therefore preferable to allow the dissolution to proceed over several days. The resulting solution is initially brick-red in color and gradually becomes emerald green and finally blue over the course of several days. If the brick-red solution is diluted with

a moderate amount of water, the liquid becomes green, exactly like the solution aged for several days. If the green solution is diluted with water, it develops a beautiful sky-blue color. If the brick-red solution is heated, it first takes on a dirty yellow shade, then green, and finally a beautiful blue-green color. If ethyl alcohol is added to the blue solution, it becomes green; as the alcohol evaporates, it turns blue again. Sugar added to the blue solution likewise causes it to become green.
If H_2O_2 is added to the green hydrochloric solution obtained above, it turns brick-red and chlorine gradually begins to be evolved.
If a large amount of sodium carbonate is added to the green solution until effervescence ceases, a fine yellow-brown precipitate is obtained.
If zinc powder, or even a piece of zinc metal, is added to the green solution, the color gradually changes to pale green, then mauve, and may even become colorless. This reaction is naturally accompanied by a vigorous evolution of hydrogen because of the acid present in the solution.
If a tannin solution is added to the green solution, a mauve coloration is obtained, followed by a blue one.
If a solution of potassium ferrocyanide is added to the green solution, a green precipitate is obtained.
Bromine water added to the hydrochloric solution of vanadium pentoxide gradually colors it yellow.

- A little-known fact: fragments of gold leaf disappear within a few tens of minutes in the green hydrochloric solution of vanadium pentoxide. The reaction no longer occurs once the solution has become blue.

- An aqueous solution of vanadium pentoxide acidified with H_2SO_4 develops a beautiful blue color when sulfurous acid is added. Alcohol gives it a raw sienna-yellow coloration.

- Vanadium pentoxide is dissolved, while hot, in a solution of NaOH and the mixture is allowed to cool. A colorless solution of sodium vanadate is thus obtained. If a tannin solution is added to this solution, an orange coloration appears. If, to the same colorless solution, an acid such as HCl, H_2SO_4, or HNO_3 is added little by little, the color changes to golden yellow and then to dark yellow before finally becoming colorless. Nothing similar occurs, however, with acetic acid. Place the same colorless sodium vanadate solution in two different test tubes. To the first, add a few drops of H_2O_2. To the second, add a few drops of H_2O_2 mixed with H_2SO_4. The first solution becomes yellow and foams slightly. The second foams strongly and, after briefly becoming mauve, also turns yellow. Then, slowly, both solutions fade.

- If a little HCl is added to the sodium vanadate solution until a golden-yellow coloration is obtained, and a solution of ammonium sulfide is then added little by little, the color changes from yellow to orange-red, then blood-red, and finally brown.
If, however, ammonium sulfide is added directly to the colorless vanadate solution, a cherry-colored V_2S_3 sulfide is formed. This combines with an excess of ammonium

sulfide to form a sulfosalt.

- Into a neutral aqueous solution of sodium vanadate, pour an aqueous solution of lead acetate. A lemon-yellow precipitate is obtained. If HNO_3 is then added, a perfectly transparent yellow liquid is produced.

- Prepare, in the cold, a solution of vanadium pentoxide in concentrated H_2SO_4. The color of this solution also evolves from day to day. The pentoxide dissolves slowly while the solution becomes orange and then orange-red. Later, once the vanadium has dissolved, the color becomes paler and shifts toward yellow-orange. This solution will hereafter be referred to as the "yellow-orange solution".
If the yellow-orange pentoxide solution is heated, it turns red while a plume of SO_3 escapes.
Add a little sugar to this slightly diluted yellow-orange solution and heat it. After a few minutes, the solution turns a delicate blue.
Pour a small quantity of this yellow-orange solution into approximately the same volume of water. The yellow color disappears immediately. Then add a little zinc powder. As the zinc reacts with the acid, the liquid becomes a beautiful pale blue and then slowly changes to a light mauve.
If the yellow-orange solution is added dropwise and carefully to a well-stirred NaOH solution until complete neutralization is achieved, the solution first becomes milky and then gradually becomes completely transparent. If this colorless solution is then poured carefully into ethyl alcohol, it turns lemon yellow.

- A solution of sulfurous acid poured into the sulfuric solution of vanadium pentoxide immediately produces a change in color. Its original yellow color changes first to pale green and then to sky blue.

- A solution of vanadium pentoxide in dilute H_2SO_4 has a beautiful light-yellow color. It becomes blue when an acidified aqueous solution of $SnCl_2$ is added. This tin(II) chloride solution must be prepared immediately before the experiment, as it does not keep.

- Vanadium pentoxide dissolves only very slightly in water (in fact, in about one thousand times its weight of water), giving it a lemon-yellow color. This solution is often referred to as "vanadic acid".
If a solution of ammonium sulfide is added to this solution, the liquid turns a cherry-orange-brown color.
If an aqueous solution of tannic acid is added to the same lemon-yellow solution, a green coloration is obtained which gradually changes to a very deep blue.
If a few drops of hydrogen peroxide are added to the same yellow aqueous solution, and in another sample a few drops of hydrogen peroxide mixed with H_2SO_4 are added, decolorization is observed, occurring more rapidly in the second case.
The same yellow solution becomes completely colorless within a few minutes when mixed with an aqueous solution of SO_2 (sulfurous acid H_2SO_3).
If a sodium-mercury amalgam is dropped into the same yellow aqueous solution,

vigorous foaming occurs and the liquid gradually becomes colorless.
Finally, the aqueous solution reacts, like other salt solutions, with various reagents such as potassium ferrocyanide or barium chloride to form precipitates of various colors.

HOW TO PREPARE AMMONIUM VANADATE

Into a 1-liter beaker placed on a heated magnetic stirrer, pour 400 mL of water and dissolve 25 g of sodium carbonate while stirring and heating. Once all the carbonate has dissolved, gradually add 4.8 g of vanadium pentoxide. The liquid, initially brown, gradually assumes a greenish goose-dropping color. Sodium metavanadate has been formed. Bring the solution to a boil and add solid sodium carbonate until the color of the liquid begins to shift toward a more yellowish green. Then gradually pour into this hot liquid 25 g of ammonium chloride previously dissolved in 80 to 90 mL of water. The liquid foams briefly with each addition of ammonium chloride and gives off an odor of ammonia. Finally, pour the whole into a 500 mL bottle whose cap is only partially screwed on, allowing gas exchange with the atmosphere. Gradually, as the liquid cools, the walls of the bottle become coated with crystals of ammonium vanadate, which is only sparingly soluble in cold water. Allow the mixture to stand overnight in an ordinary refrigerator, then pour the liquid into a second bottle similar to the first. Rinse the walls of the first bottle with distilled water. The walls are now completely covered with small white crystals of ammonium vanadate, which is only slightly soluble in water. Pour approximately 60 mL of H_2SO_4 into this bottle and rotate it so that the acid thoroughly wets the walls. The crystals immediately turn yellow and then blood red, while the bottle becomes strongly heated. Once all the crystals have disappeared and the contents of the bottle have become a clear blood-red liquid, pour it gradually into 200 mL of water while stirring, since a further rise in temperature occurs. A canary-yellow sulfuric solution of ammonium vanadate is thus obtained. The second bottle is then reheated to boiling and ammonium chloride is once again added as before, after which the solution is allowed to cool. This second operation may allow a further quantity of ammonium vanadate to be recovered by proceeding in the same manner.
Carry out the preceding experiment up to the point where, after cooling in a refrigerator, the walls of the bottle are covered with fine white crystals. Pour off the liquid, which may be treated as described above, and quickly rinse the bottle with water. Then pour 150 to 200 mL of water into the bottle containing the crystals and place it on a magnetic stirrer. A milky liquid is obtained which, when removed from the stirrer, rapidly deposits a white "paste". This stirring operation is repeated many times over a period of three or four days because ammonium vanadate dissolves only very slowly in water. Finally, decant to obtain a colorless aqueous solution of ammonium vanadate.

- If a drop of sulfuric acid is added to the colorless aqueous solution of ammonium vanadate, the solution immediately turns yellow, proving that it contains vanadate.

- If a little acetic acid is added to the colorless solution of ammonium vanadate, the

solution immediately becomes reddish owing to the formation of an acid vanadate. The same result can be obtained with various other acids. However, if a solution of sulfurous acid is used, a beautiful blue V_2O_4 tetroxide slowly forms.

- In the colorless aqueous solution of ammonium vanadate, an aqueous solution of silver nitrate produces a cloudy dark-yellow precipitate.
The same occurs in an aqueous solution of ammonium vanadate mixed with H_2SO_4, but in this case the cloudy precipitate is lemon yellow.

- Pour a colorless solution of ammonium vanadate, add a solution of sulfurous acid. The solution becomes yellow, then very rapidly green, and finally sky blue.

- Add a few drops of hydrogen peroxide to a colorless solution of ammonium vanadate. The solution acquires a canary-yellow color. In another ammonium vanadate solution, add a few drops of hydrogen peroxide mixed with H_2SO_4. The solution becomes orange. If each of these solutions is heated, their colors become noticeably darker and then, upon cooling, both become canary yellow. A few drops of hydrogen peroxide mixed with H_2SO_4 cause the second solution to become orange to red once again.

- A solution of ammonium vanadate poured into a solution of copper sulfate gives a precipitate of copper orthovanadate having a goose-dropping color. However, if it is allowed to stand, it appears rather whitish in a liquid that has become yellowish green. If the mixture is heated and the copper salt is present in excess, the precipitate becomes more yellow while the liquid becomes bluish. If, on the contrary, the vanadate is present in excess, the precipitate dissolves.

- If a strip of magnesium is placed in the colorless aqueous solution of ammonium vanadate, the solution gradually changes color. Depending on the quantities present, it becomes either olive green or pale blue.

- Pour a freshly prepared aqueous solution of tannic acid into an aqueous solution of ammonium vanadate that is as concentrated as possible. An ink-black liquid is obtained immediately. If chlorine water is then added slowly to this liquid while stirring, it gradually becomes dirty yellow, then canary yellow, and finally, with time, colorless. The addition of hydrochloric acid before complete decolorization may gradually produce a pale-green coloration. I have also noted that the canary-yellow color may sometimes persist if the original reacting solutions are only weakly concentrated. If, instead of chlorine water, a little hydrochloric acid or a solution of caustic soda is added to the black solution, a reddish-brown coloration gradually develops in both cases and may evolve into blue-green over the course of several hours.

- If an aqueous solution of sodium sulfite is poured into the canary-yellow sulfuric solution of ammonium vanadate, the color changes to sky blue.

- If a little zinc powder is added to the canary-yellow sulfuric solution of ammonium vanadate, the solution rapidly becomes blue and then, upon further stirring, mauve. Finally, after many hours, it becomes green.

- If an aqueous solution of potassium ferrocyanide is poured into the canary-yellow sulfuric solution of ammonium vanadate, a heavy dark-green precipitate is obtained.

- If the canary-yellow sulfuric solution of ammonium vanadate is poured onto a little mercury and shaken, a precipitate forms which, after standing, appears white while a duck-blue or greenish liquid floats above it.If some mercury still remains, it will be seen to have acquired a dull, spongy appearance. In fact, it then consists of very small droplets mixed with the precipitate. If the mercury is thoroughly washed to remove all traces of the other substances, it regains its usual appearance.

- If two or three drops of mercury that has long been in contact with zinc are introduced into the acidified canary-yellow solution of ammonium vanadate, a coloration gradually appears in the tube. At first green and diffuse, it becomes increasingly blue over the course of several days, with layers of yellow, green, blue, and mauve corresponding to the different valence states of the metallic ion (Figure 135). After many days, the solution becomes entirely blue.

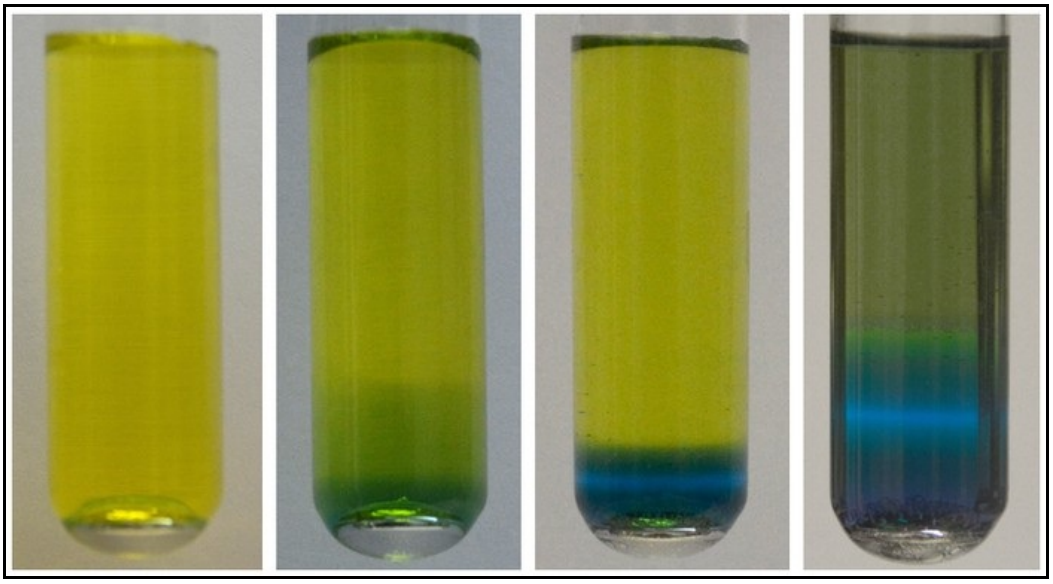


Figure 135

Titanium Salts

- In a flask of approximately 250 mL capacity, titanium oxide TiO_2 is heated in concentrated sulfuric acid for about twenty minutes. To prevent violent bumping of the liquid, a few fragments of pumice stone should be added to the flask. If white SO_3 fumes are evolved, the heat input should be reduced slightly and then increased again afterward. This done, allow the mixture to cool and settle in a large test tube. A yellowish liquid eventually forms an upper layer. It may be regarded as a sulfuric

solution of titanium sulfate in which the titanium sulfate is present in relatively low concentration compared with the acid.
Pour two drops of this solution into distilled water, stir, and then add H_2O_2. A beautiful yellow-orange coloration is obtained owing to the formation of peroxytitanic acid. This reaction is so sensitive that titanium sulfate in solution is used to detect very small quantities of hydrogen peroxide in a liquid.
If a little ammonia is added to this yellow-orange liquid, it becomes colorless again.

- By heating titanium in concentrated hydrochloric acid, a mauve-violet hydrochloric solution of titanium chloride may be obtained. The following reactions may be carried out with this solution:
Methylene blue and potassium permanganate in aqueous solution are decolorized instantly.

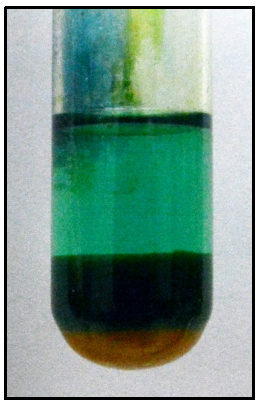


Figure 136

With a solution of NaOH, KOH, or NH_4OH, it gives a very dark blue, almost black, gelatinous precipitate.
In a solution of potassium ferrocyanide, it produces an orange-brown precipitate; however, after several days, this precipitate is found beneath a second, darker one, itself surmounted by a liquid layer of a beautiful dark emerald-green color (Figure 136).
With a solution of iron(III) chloride, it gives an orange-brown precipitate that undergoes no subsequent change.
When poured into a solution of ammonium molybdate, the hydrochloric solution gives a gray-blue precipitate which becomes completely blue upon stirring.

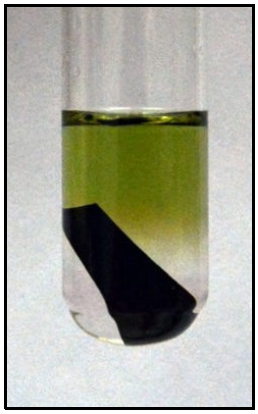


Figure 137

Zinc powder reacts with it to evolve hydrogen, and it is therefore necessary to wait until this reaction has ceased before observing that a blue precipitate has formed.
A copper strip decolorizes the solution very gradually and, over the course of several days, becomes coated with a black film while the liquid, if left undisturbed, acquires a blue-green coloration. At first, simple stirring is sufficient to change the color to a very pale yellow; however, this yellow appearance is actually a pale green that gradually intensifies over the course of several days (Illustration 132). After a considerable time, the color becomes dirty yellow and then goose-dropping green.

Molybdenum Salts

Molybdenum salts may exhibit five different oxidation states:
+2 (mauve-violet)
+3 (green)
+4 (blue, or brown to black for alkaline derivatives)
+5 (red-brown)
+6 (colorless)

Several oxidation states often coexist in the same reaction mixture, so that, depending on numerous factors, an entire range of different colors may be obtained. Here, then, is yet another "mineral chameleon" fully worthy of comparison with that of vanadium!

- Molybdenum(VI) oxide is poured into HCl. A mixture gradually forms with a white solid portion that eventually disappears (within 24 hours), leaving only a perfectly colorless liquid. A hydrochloric solution of the trioxide has thus been prepared, which I shall call, for convenience, "A".
The following reactions may be obtained with solution "A":
A little hydrogen peroxide produces a yellow coloration that disappears after boiling and complete release of the oxygen.
A little zinc powder produces effervescence and a yellow, green, or blue coloration, depending on the amount of zinc used. When hydrogen is no longer being evolved, add a few drops of H2O2 . The solution then becomes canary yellow. Heat it in a test tube while shaking. The yellow color disappears while a white powder deposits on the cooler walls of the test tube. If, after a while, this powder is mixed back into the liquid portion, the latter takes on a dark yellow tint.
With a little iron powder, the liquid immediately becomes green. If the solution has first been diluted, the color obtained is instead yellow.
If a piece of nickel is placed in it, a green liquid halo gradually forms around the metal. If the liquid is stirred, the green coloration progressively spreads throughout the entire solution. If the solution was diluted beforehand, the color first obtained is canary yellow and then becomes yellow ochre.
If a piece of arsenic is placed in it, the liquid turns green only very slowly. If the solution has been diluted beforehand, a yellow solution is once again obtained.
If a piece of aluminum is placed in it, the reaction begins slowly at first and then rapidly becomes vigorous. The color soon changes from green to wine red.
If ammonia is gradually added until it predominates over the acid and a few drops of hydrogen peroxide are then added, a yellow-red coloration is obtained which gradually disappears as oxygen is evolved.
If a few crystals of potassium iodide are added, a reaction already occurs in the cold. When heated, the reaction becomes more vigorous: an orange liquid tending toward brown is obtained, and iodine is eventually liberated. Potassium iodide heated in HCl does not produce this color.
If a solution of potassium thiocyanate is added, an orange-red color is obtained.
If a solution of potassium ferrocyanide is added, a red to brown precipitate is obtained. Nothing, however, is produced with potassium ferricyanide or potassium chromate (which darkens in shade because it becomes dichromate in the acidic medium).
If a few drops of a sodium sulfide solution are added, a red-brown precipitate is obtained and a strong odor of H_2S becomes noticeable owing to its reaction with the acid.
If a hydrochloric solution of tin(II) chloride is added, a green opalescent liquid is obtained.

- Place solution A in three test tubes. Add a lead shot to the first, a tin shot to the second, and two drops of mercury to the third. The reaction is vigorous with tin, and the entire liquid rapidly turns green, then brick-brown, and finally a beautiful red. With lead, the reaction is much slower; a green layer first appears, followed by an orange layer that eventually spreads throughout the liquid. With mercury, the reaction is extremely slow, but the green coloration eventually appears after two or three hours (Figure 138). In less than 24 hours, the first two tubes have become red, whereas the third is only slightly green. Heating the third tube greatly accelerates the reaction. The same remark applies to the other two reactions, although their progression then becomes less visible.

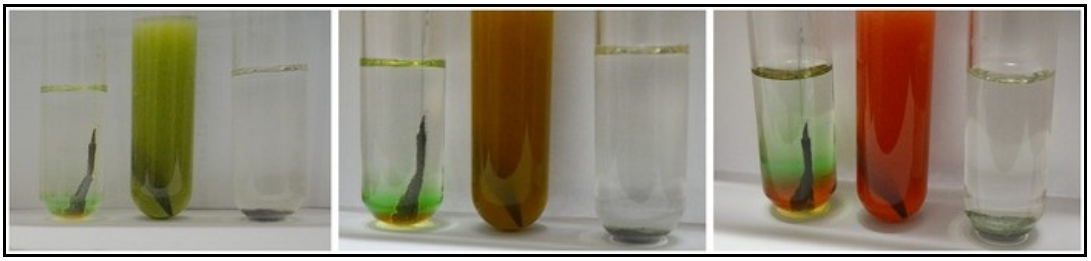


Figure 138

Figure 139

As stated above, when a tin shot is placed in solution A, the liquid rapidly becomes green and then gradually turns red. However, if solution A has first been diluted, the liquid quickly becomes lemon yellow and then evolves toward yellow ochre. The same result is obtained if the tin is replaced by antimony. It should be noted that, in this case, if the flask is not stirred, two layers gradually appear: at the top, a beautiful green layer, and at the bottom, around the antimony, an orange-red layer (Figure 139). In time, however, the substances mix and the liquid becomes entirely red.

Let us repeat the previous experiment with a hydrochloric solution of molybdenum trioxide, but this time add two or three drops of H_2O_2 before introducing the mercury. The liquid immediately becomes yellow-orange. Only then is the Hg added. During the following 48 hours, a green tint appears above it, while the orange coloration gradually fades into a pale yellow.

- Place a more-than-saturated hydrochloric solution of molybdenum trioxide in a test tube, that is, one containing undissolved trioxide. Add one drop of mercury and wait several hours, shaking periodically. The reaction is very slow and is best continued for 24 hours. Gradually, the solution becomes yellow-green and then increasingly yellow over the following days. The trioxide is in fact being converted into molybdenum trichloride.

- Take four test tubes and pour 3 to 4 centimeters of concentrated HCl into each. Divide them into two groups. Into one test tube of each group, add a little

molybdenum trioxide and shake to disperse it. Then place a piece of lead into each tube of the first group and a piece of tin into each tube of the second group. Gas evolution is observed in all four test tubes. Twelve hours later, the gas evolution has ceased. A pink coloration is observed wherever the trioxide had been added.

- Instead of mixing molybdenum trioxide with HCl, it may be mixed with a NaOH solution. It dissolves immediately, forming an alkaline solution of sodium molybdate. If potassium ferrocyanide, potassium ferricyanide, potassium thiocyanate, or sodium sulfide is added to this solution, nothing apparent occurs. However, if a few drops of hydrogen peroxide are then added to each test tube, the liquid in each acquires a light red to dark red color that disappears as oxygen is expelled by shaking or heating. The same red coloration appears in the original solution, especially if a trace of H_2SO_4 is added.

- If a hydrochloric solution of tin(II) chloride is added to the alkaline sodium molybdate solution, a slightly orange-yellow opalescent liquid is obtained.
If a little zinc powder is added, gas evolution occurs and the solution remains colorless provided the NaOH concentration is high. However, if HCl is added in order to neutralize the NaOH rapidly, gas evolution intensifies and the liquid gradually changes from yellow to brick red.

Molybdenum trioxide dissolves very slowly in cold water and only in small amounts, thus forming a solution of molybdic acid, which I shall hereafter designate, for convenience, as "MA".
The following reactions may be obtained with this "MA" solution:
If a slightly warmed aqueous solution of tannic acid is added (warmed so that the tannin dissolves properly), the mixture changes from colorless to yellow and then to orange.
If a few drops of logwood tincture are added, a mauve-lilac coloration is obtained.
If a little zinc is added, it is gradually attacked while the color shifts slightly toward yellow. Heating greatly accelerates the reaction. The addition of H_2O_2 renders the liquid colorless. However, if a little aqueous NaOH is added before the H_2O_2, a beautiful yellow liquid tending toward orange is obtained. If, however, one or two drops of HCl are added after the zinc powder has been introduced, the reaction proceeds more rapidly and the color quickly turns to a dirty yellow. Heating greatly accelerates the gas evolution. The subsequent addition of H_2O_2 makes the liquid completely transparent. But if a little aqueous NaOH is added before the H_2O_2, the addition of H_2O_2 first produces a beautiful yellow liquid tending toward orange and then, as more reagent is added, a precipitate of the same color.
If a little molybdenum powder is digested in the MA solution while being carefully protected from air, an intensely blue liquid, resembling ink, is gradually obtained. This was formerly called molybdous acid or molybdenum blue. It is in fact a combined solution of MoO_3 and Mo_2O_5. Berzelius stated that this liquid eventually became red and that he then obtained hydrated molybdenum dioxide (that is, a hydroxide in the old nomenclature) by precipitating the oxide formed with ammonia. For my part, I was unable to obtain the red liquid even after more than

fifteen days, and I observed that ammonia rendered the blue liquid colorless.

- If a piece of tungsten is placed in the MA solution, a blue coloration appears very slowly around the metal, especially visible when the flask is gently agitated. More than 24 hours are required before this coloration begins visibly to spread throughout the entire liquid. After 48 hours, it finally becomes a beautiful steel blue. Periodic, or even continuous, agitation appears to facilitate the process. The same result, however, is obtained at the boiling temperature in about twenty minutes.

- If one drop of a potassium dichromate solution is added to the MA solution, an emerald-green coloration is produced which subsequently turns canary yellow. Heat accelerates this reaction.

- In the MA solution, one drop of bromine water first produces a green coloration which then turns yellow. Upon heating, the solution becomes colorless.

- In the MA solution a potassium ferrocyanide solution produces a green coloration which soon intensifies into a beautiful emerald green. When heated, this solution turns olive green and, upon cooling, returns to emerald green. Then, over the course of several days, it changes to duck-egg blue, and if a few drops of HCl are added, a black precipitate is obtained.

- In the MA solution a solution of iron sulfate causes a gradual change to pale green and then, with time, the liquid becomes completely colorless.

- In the MA solution a little hydrochloric solution of antimony trichloride produces a bluish-white precipitate which dissolves in HNO_3 to give a yellow liquid.

- In the MA solution, the combined addition of a little HCl and copper powder produces a gradual yellowing over several days. Then, after this lengthy "maturation," the copper suddenly begins to disappear rather rapidly and the liquid acquires a green tint. Subsequently, by adding a little more copper, the metal disappears within a few hours while producing a deeper green coloration. The remarkable feature of this reaction is therefore the lapse of time required for its maturation. I have observed that if too much copper is added, the color reverts permanently to a dirty yellow.

- If a little $SnCl_2$ powder is added in the MA solutiuon and the mixture is shaken, a yellow liquid is immediately obtained. This very rapidly turns into a cloudy goose-green liquid and then, after some time, changes to pale green and finally to lavender blue.

- If an aqueous solution of lead acetate is added in the MA solution, a white gelatinous precipitate is obtained, sometimes showing a slight yellow tint depending on the concentrations.

- If the MA solution is gradually added to an aqueous solution of potassium ferrocyanide, the initial pale-yellow solution becomes darker and then, slowly, after about two hours, turns pale green. If it is then heated, it becomes cloudy, turns duck green, and finally deposits a black solid.

- Molybdenum trioxide reacts with a citric acid solution by first forming, within about an hour, a true white milk. This then gradually decolorizes over several days until it finally becomes completely transparent and colorless. If a little zinc powder is added to this colorless solution, a greenish color first appears with effervescence and then changes to yellow ochre. If this latter liquid is mixed with ammonia, the color changes only slightly. It darkens further and tends toward orange if hydrogen peroxide is then added. Conversely, if hydrogen peroxide is first added to the yellow-ochre solution, almost complete decolorization occurs, followed by a return to an orange coloration when ammonia is subsequently added.

Molybdenum trioxide dissolves very slowly in phosphoric acid at room temperature until a perfectly clear liquid is obtained. More than a week of patience is required. If a little zinc powder is then added to this solution (previously diluted with an equal volume of water), a yellow liquid is rapidly obtained with effervescence, gradually becoming dirty brown. If this latter liquid is mixed with a little ammonia, it becomes strongly decolorized. The same occurs with hydrogen peroxide.

- After many days in lactic acid, molybdenum trioxide yields a yellowish liquid with a white deposit which, when shaken, forms a syrupy white milk. Mixed with H_2O_2, this white milk becomes yellowish and, when sufficient ammonia is added to neutralize the acid, ultimately gives a perfectly transparent liquid whose color tends toward yellow or orange.
If the yellowish syrupy liquid is diluted with an equal volume of distilled water and then treated with H_2O_2, it immediately develops a yellow coloration. If an aqueous NaOH solution is then added, the liquid turns orange after first appearing to become colorless.
If the original white milk is treated with a little zinc, it turns yellow. The addition of zinc powder immediately produces a yellow coloration tending toward green, which subsequently evolves into goose-green and then dirty brown.
The solution of molybdenum trioxide in lactic acid possesses a characteristic not shared by solutions of the trioxide in other acids. Indeed, a few drops of logwood tincture added to a given quantity of lactic acid produce a yellow coloration, whereas the same number of drops added to the same quantity of the yellowish liquid produce a distinctly reddish coloration.

- Molybdenum trioxide dissolves only when heated in concentrated sulfuric acid. Upon cooling, a slightly yellow liquid is obtained. If this is diluted with an equal volume of water and a little zinc powder is added, the liquid becomes more intensely yellow. If the zinc powder is added to the concentrated liquid, a kind of grayish-green gelatinous milk is formed which, after a few tens of minutes, yields a bluish-green liquid.

If, instead of zinc powder, a strip of zinc is placed in the liquid, the reaction begins very slowly, and little by little a turquoise-blue zone appears at the bottom of the test tube. If a little aqueous sodium thiocyanate solution is added to the diluted solution, a golden-yellow color is obtained which subsequently fades gradually (Figure 140).

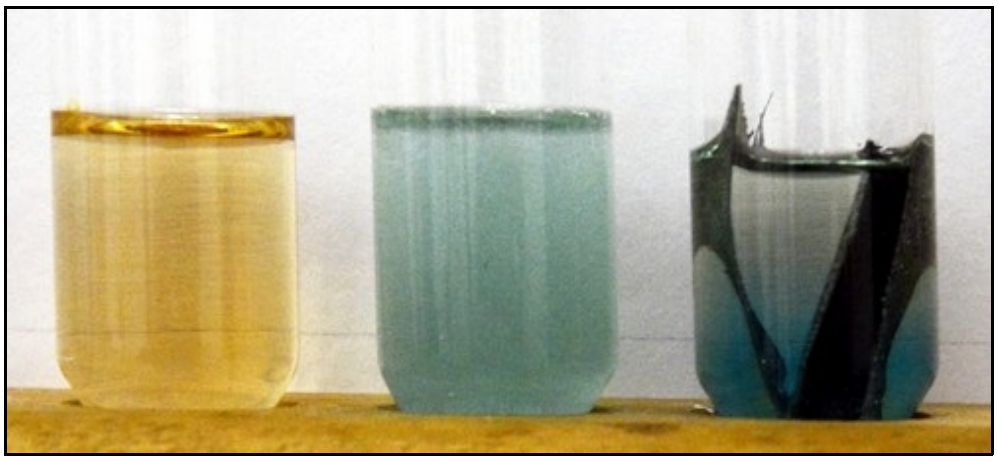


Figure 140

- In a test tube, place two or three centimeters of an aqueous solution of molybdenum trioxide (or sodium molybdate). Carefully pour a solution of potassium thiocyanate (sulfocyanate) on top. Nothing appears to happen. Then add a few drops of HCl. The liquid develops a beautiful yellow or orange color, depending on the quantities involved. Add one or two centimeters of ether and shake. The yellow-orange color passes into the ether and becomes concentrated there. Molybdenum thiocyanate has been formed.

- Molybdenum trioxide dissolves in oxalic acid at room temperature within 24 hours. The addition of a little H_2O_2 to this liquid produces a slight yellow coloration. If ammonia is then added, the color changes from yellow to orange with vigorous evolution of O_2 and noticeable warming.
The addition of a little zinc powder to the original liquid immediately causes it to turn yellow or brown, depending on the amount of zinc used.

- It is convenient to purchase crystalline ammonium molybdate from specialized suppliers. Nevertheless, it may be obtained in solution as follows: molybdenum trioxide is poured into a concentrated ammonia solution. The trioxide disappears rapidly, leaving a clear colorless liquid. Heat until the excess ammonia gas has completely disappeared, then allow the solution to crystallize on a radiator or by means of a laboratory hot plate.
CAUTION: an aqueous solution of ammonium molybdate is altered by light. It should therefore be stored in an inactinic bottle. The presence of certain substances accelerates this decomposition. For example, if a test tube containing an aqueous solution of ammonium molybdate to which one drop of lactic acid has been added is placed in full sunlight, the initially colorless liquid becomes blue within about ten

minutes. See also Chapter 13 on photochemical reactions.

- Prepare an aqueous ammonium molybdate solution containing a small amount of nitric acid. Then add phosphoric acid. A beautiful yellow color develops but disappears in the presence of an excess of acid.

- Add a little powdered tin chloride to an ammonium molybdate solution and shake. The liquid takes on a goose-green color which gradually changes into peacock green.

- If an aqueous solution of tin(II) chloride acidified with HCl is added to a solution of ammonium molybdate acidified with HNO_3, a beautiful blue precipitate of molybdenum trioxidectoxide, Mo_3O_3, is obtained. The addition of water and glycerol yields a beautiful transparent blue liquid which gradually becomes lighter as it is oxidized by air. The addition of HNO_3 or ammonia leaves a transparent liquid.

- A nitric solution of mercuric nitrate produces a white precipitate in an ammonium molybdate solution.

- Prepare a 10% ammonium molybdate solution and add an equal volume of concentrated H_2SO_4. This liquid will gradually become bluish under the action of light, but it may be used before this occurs. If poured into H_2O_2 , a yellow coloration is obtained. If a small amount of HNO_3 is added and the mixture is warmed slightly, the reaction generally becomes vigorous.

- Prepare a concentrated hydrochloric solution of ammonium molybdate. It is colorless. Add a little molybdenum powder. Gradually, the liquid acquires a beautiful emerald-green color. If this liquid is then diluted with distilled water, it takes on a beautiful yellow-ochre coloration. If an aqueous NaOH solution is added to the latter, a brown precipitate is obtained.

- Prepare a solution of ammonium molybdate (or sodium molybdate). Drop in a well-cleaned piece of copper. Nothing happens. Add one or two drops of HCl. A film immediately forms on the copper. If the liquid is stirred, the film dissolves and produces a beautiful deep blue liquid resembling Prussian blue. If a little NaOH solution is added, the blue color disappears immediately. The same occurs with a little H_2O_2 , but a slight yellow coloration remains and subsequently intensifies as oxygen is evolved.

- If a solution of iron(II) sulfate is gradually added to an ammonium molybdate solution, a precipitate of mastic color forms immediately. Stir the liquid and precipitate, then divide the mixture into four portions. Heat the first portion in a test tube: the color becomes darker and settling is accelerated. Treat the second portion with HCl added dropwise. After bluish shades appear throughout the mixture, the liquid ultimately becomes slightly yellow and transparent. If a few drops of H_2O_2 are then added, O_2 is evolved and the liquid becomes much more yellow. Treat the mastic-colored precipitate of the third portion with a few drops of H_2SO_4. The liquid

Figure 141

now becomes completely transparent and colorless. If a few drops of H_2O_2 are added, it turns yellow. Treat the mastic-colored precipitate of the fourth portion with HNO_3. The liquid first becomes olive-colored, then brownish, and finally becomes lighter, retaining only a faint yellow color. If a few drops of H_2O_2 are added, the yellow color intensifies. If a strip of zinc is dropped into the test tube containing the intensely yellow liquid obtained from the precipitate that had reacted with hydrochloric acid and then hydrogen peroxide, abundant foam first appears. Gradually, the gas evolution decreases while an off-white precipitate appears and slowly settles. After several hours, a second precipitate appears, orange this time, and settles above the first one (Figure 141).

- Place an aqueous solution of salicylic acid in a test tube and add a few crystals of ammonium molybdate. Soon, the liquid around the crystals becomes canary yellow. The mixture may be stirred from time to time to distribute the coloration more evenly.
If two aqueous solutions, one of the acid and the other of the molybdate, are brought together directly, the effect is less readily visible.

- Add a little sodium phosphate solution to an ammonium molybdate solution. Nothing happens. Then add HCl drop by drop. The solution turns yellow. If a small spatula-tip quantity of zinc powder is introduced into this liquid, the solution immediately turns blue. If H_2O_2 is then added to the blue liquid, it turns green and then slowly yellow, depending on the concentrations involved.

- Add a little sodium silicate solution to an ammonium molybdate solution. The solution immediately acquires a faint yellow coloration, which becomes much more intense upon the addition of a few drops of HCl. If very little zinc powder is added to this latter solution, a blue liquid together with a brown precipitate is obtained. Addition of H_2O_2 first turns the liquid green and then yellow while causing the precipitate to disappear.

- Add a little manganese chloride solution to an ammonium molybdate solution. The colorless solution immediately becomes pale yellow. If a few drops of HCl are then added, it immediately becomes colorless again.
If, instead of HCl in the preceding experiment, a NaOH solution is added, a precipitate is obtained whose color differs somewhat from that produced by NaOH in manganese chloride alone.

- Prepare an ammonium molybdate solution as described above. While stirring, pour a fairly large quantity of aceton into it. A precipitate forms and soon settles to the bottom of the test tube. Decant and dissolve the precipitate in water (heating if necessary). Add one or two drops of H_2SO_4 and then introduce a strip of magnesium two to three centimeters long. A strong foam develops while the liquid becomes a deep blue.

- Pour equal quantities of a colorless aqueous ammonium molybdate solution into two test tubes. Add a little glucose to the first and a little menthol to the second. Nothing happens. Then add a few drops of concentrated HCl to each. Again, nothing happens. Finally add a small amount of zinc powder to each test tube and shake gently. Both liquids immediately turn blue. If a few drops of H_2O_2 are then added to each tube, the blue color gradually disappears, sometimes forming a beautiful cloud and leaving behind, together with a foaming gas evolution, a beautiful transparent golden-yellow liquid. The same experiment may be carried out using a strip of zinc in order to show more clearly that no precipitate forms at any stage (Figure 142).

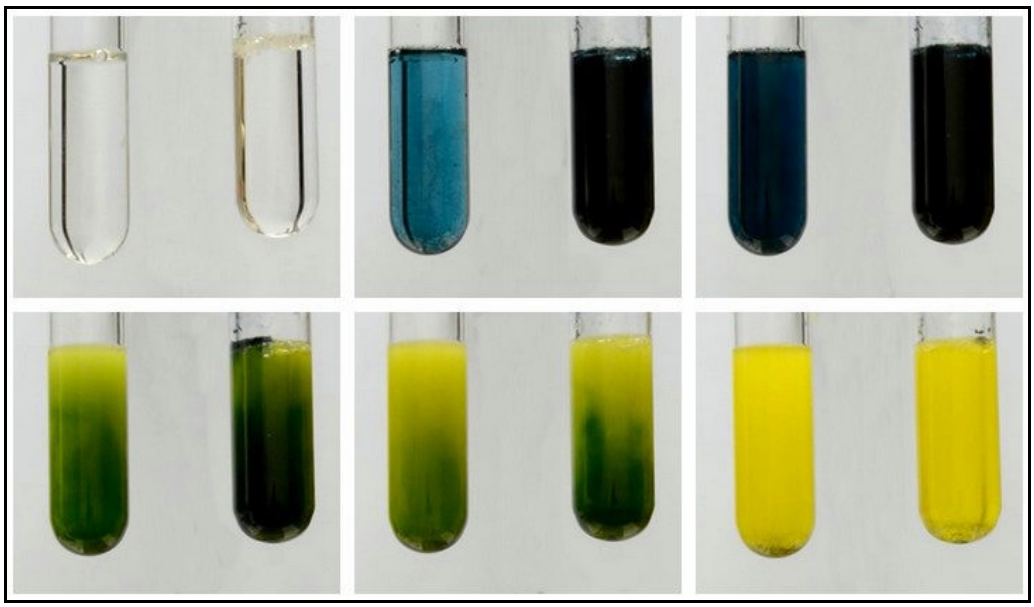


Figure 142

- Add a small amount of hydroquinone to an ammonium molybdate solution and shake. If necessary, warm gently until the hydroquinone has dissolved completely. The liquid then acquires a very faint yellow tint. Concentrated HCl is then added progressively, drop by drop. The liquid successively turns green, then an increasingly intense blue, before finally becoming green again and ultimately yellow.

- Pour an aqueous ammonium molybdate solution into a solution of an alkaline arsenate acidified with HNO_3. A yellowish precipitate forms, especially when heated. It is preferable, however, to pour the arsenate solution into the molybdate solution.

Tungsten Salts

- In a test tube, place a little 100-volume hydrogen peroxide and then add a small spatula-tip quantity of tungsten carbide. The reaction begins slowly and gradually increases in intensity. Gentle warming at the beginning may help initiate it. The carbide eventually disappears completely in the liquid. Add more until the reaction ceases and some carbide remains unaltered. Carbon dioxide, water, and tungsten trioxide, WO3, have been formed. In contact with water, the latter produces tungstic

acid, H_2WO_4 . Divide the liquid into two portions. Add a few drops of NaOH to the first. A yellow coloration is obtained. To the second, add two drops of HCl followed by a small spatula-tip quantity of zinc powder. The beautiful blue coloration characteristic of tungsten pentoxide, W_2O_5 , is then obtained.

- The yellow tungsten trioxide obtained by the action of aqua regia on tungsten when heated (see Chapter 14.1) dissolves completely in ammonia, even when the latter is not very concentrated, forming ammonium tungstate. If concentrated HCl is gradually added to this transparent colorless liquid while allowing the white fumes formed to escape, a pale yellowish-white precipitate is obtained which eventually turns blue.

- If tungsten trioxide is dissolved in a NaOH solution, a little zinc powder is added, and concentrated HCl is then introduced drop by drop until the NaOH has been neutralized and the zinc powder begins to effervesce, the entire liquid rapidly turns blue owing to the formation of a fine precipitate of that color. This precipitate disappears completely upon the addition of a few drops of H_2O_2.

- If tungsten trioxide is dissolved in a NaOH solution and a hydrochloric solution of tin(II) chloride is then added, a dirty-white gelatinous precipitate gradually forms and eventually becomes blue.

Borates and Perborates

- Add a solution of barium chloride to an aqueous solution of an alkali borate. A white precipitate is obtained, soluble in acids.

- In an aqueous solution of an alkali borate, silver nitrate produces a precipitate whose color may vary from white to brown depending on the concentrations.

- In the water-soluble solutions of copper, zinc, lead, cobalt, nickel, or manganese salts, an aqueous solution of sodium tetraborate produces a gelatinous precipitate in every case.

- The same experiment carried out with a hot solution of sodium perborate gives much more visible results, generally accompanied by colored precipitates and the evolution of a gas.

Antimony Salts

- Slowly add water, with stirring, to a hydrochloric acid solution of antimony chloride. A white precipitate of oxychloride gradually forms. It is soluble in an excess of HCl or in tartaric acid.

- Prepare a solution emetic, which contains antimony tartrate. Hydrochloric, sulfuric, and nitric acids produce precipitates of basic antimony salts that dissolve in an excess of acid.
Bases may act in the same way, but much depends on the concentrations involved. Tannic acid also produces a precipitate.
H_2S transforms the emetic solution into a beautiful golden-yellow to red liquid, depending on concentration. If a few drops of a mineral acid are added to this liquid, a red sulfide precipitate forms.

- If a little iodine tincture is added to an alcoholic solution of emetic, a color change toward yellow is observed. If the liquid is then allowed to evaporate, crystals of antimony iodide are obtained.

- Slowly add a hydrochloric acid solution of antimony chloride to ammonia. A white precipitate forms and is soluble in HCl.

Arsenates and Arsenides

- Arsenates are identified by the red precipitate they form with silver nitrate.

- Slowly add a solution of $AgNO_3$ to a solution of an alkali arsenate. A brick-red precipitate appears. It is soluble in HNO_3 or ammonia.

- Dissolve arsenious oxide in concentrated hydrochloric acid. The liquid becomes yellow. Its composition appears to be variable. It may be regarded as arsenic chloride, which decomposes if mixed with water.

Other Types of Mineral Salts

- Prepare an aqueous solution of cerium sulfate in a test tube using water acidified with H_2SO_4 (since cerium sulfate does not dissolve in neutral water). Add two or three drops of dilute ammonia to this yellow solution. A slight whitish cloudiness appears. Then add a little hydrogen peroxide. A red-orange precipitate of ceric hydroxide forms.

- Pour an aqueous solution of cerium sulfate acidified with H_2SO_4 into a test tube. Add a little ammonium acetate solution. Decolorization is observed. Then gradually add hydrogen peroxide. A coloration appears, followed by a reddish-brown precipitate.

- Place a little calcium silicide in a test tube and then add concentrated HCl. Small yellow particles of the suboxide $Si_3H_3O_2$, formerly known as silicon, gradually form.

12.4. Reactions with Fuming Nitric Acid

Fuming nitric acid possesses very unusual properties and therefore deserves a section of its own.

This acid may be obtained from specialized suppliers; however, since its storage presents a number of difficulties and only very small quantities are generally required for individual experiments, it is usually more convenient in an amateur or school laboratory to prepare it as needed according to the procedure described on pages 117-118.

- Place a flask in an ice bath and, once thoroughly cooled, fill it with SO_2 by downward displacement (since this gas is heavier than air). Then allow a few drops of fuming nitric acid to fall into it. Crystals are deposited on the walls. They consist of nitrosyl sulfate.

- Allow a few drops of fuming HNO_3 to fall into a large flask filled with H_2S. A very brief and rather unimpressive ignition is observed, after which sulfur is deposited on the walls of the flask while NO_2 is formed within it.

- If magnesium powder is poured into fuming nitric acid, a very vigorous reaction occurs, producing a plume of reddish-brown fumes (Illustration 143).

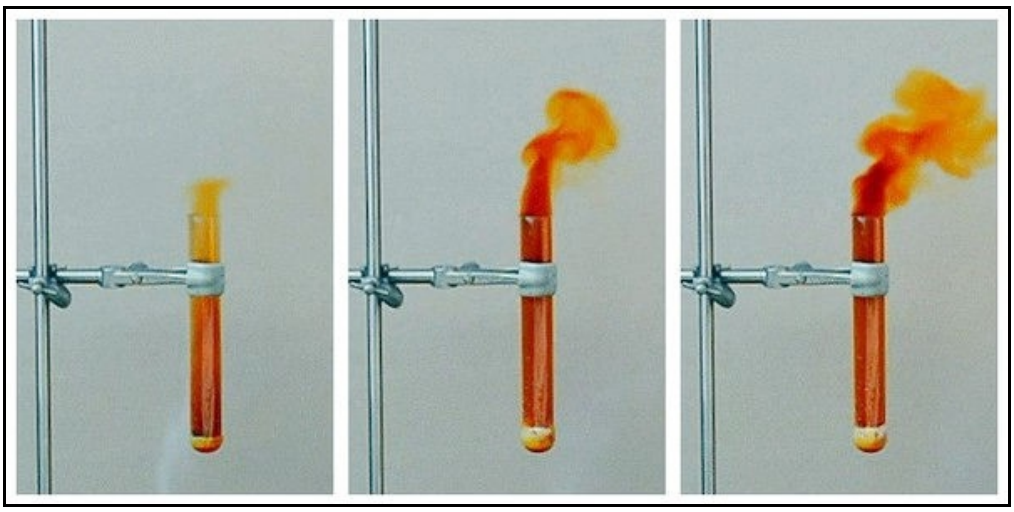


Figure 143

- Place powdered charcoal in a porcelain dish. Warm the dish until the material it contains reaches approximately 40°C. Then, using a pipette or burette, allow a few drops of fuming HNO_3 to fall onto the powder. At the point of contact of each drop, incandescent charcoal particles are projected in all directions. This spectacular experiment is nevertheless not particularly dangerous.

- Pour a few drops of fuming HNO_3 onto a latex glove. It changes color and "melts."‘ This demonstrates the uselessness of such gloves for protection against this acid.

CHEMICAL BURNS

No matter how careful one may be, it is not uncommon for dangerous chemicals to come into contact with the skin or even the eyes. In such cases, it is important never to panic and always to know what emergency measures should be taken.

Minor burns caused by acids and alkaline solutions generally reveal themselves by a tingling sensation or an itching feeling that prompts one to scratch. One should pay attention to these signs and immediately wash the affected area with plenty of water, then bathe it with a solution of sodium bicarbonate, which should always be kept readily available. If the burn is not too severe, the itching sensation should then cease.

Two acid burns are particularly feared because, at first, they do not really cause pain or irritation: burns caused by nitric acid and hydrofluoric acid.

My readers will no doubt have noticed that no experiment involving hydrofluoric acid is mentioned in the present book. **This product is indeed so dangerous that it should be completely excluded from an amateur laboratory**. Moreover, it presents so many potential dangers to glassware that one would have to be reckless to handle it in a small laboratory. It is, in fact, the product used for glass etching and which irresponsible individuals now transport in plastic bottles in order to produce particular forms of "graffiti" by frosting windows. When it comes into contact with the skin, this acid penetrates it and may even attack the bones beneath, which can make amputation necessary.

As regards nitric acid, one should be doubly cautious when handling it and avoid allowing drops to run or be projected. Should an accident nevertheless occur, cleaning should be carried out as for other acids, that is to say by first rinsing thoroughly with large quantities of water and then applying sodium bicarbonate. One should not hesitate to apply a "dressing" of moistened bicarbonate powder and leave it on the affected area for one or two minutes. In all cases, however, this acid will still produce necrosis of the skin, manifested by thickening an yellowing before the damaged tissue is eventually shed.

Burns caused by sulfuric acid are fortunately less dangerous and spectacular than those known as "vitriolization," which are produced by fuming sulfuric acid. This substance has not been discussed here either because of its dangerous nature and the difficulty of obtaining it nowadays. Burns caused by ordinary concentrated sulfuric acid should be treated in the same manner as those caused by nitric acid.

In the event of contact between the eyes and any chemical product whatsoever, the first reflex should be to flood the eye with a large quantity of water. Do not hesitate to immerse the entire head, eyes open, in a basin of water or a large sink, and then proceed to a hospital. Continuing to rinse the eye with water during the journey to the hospital is often the best thing to do.

If phosphorus comes into contact with the skin, the affected area should immediately be kept under a layer of water in order to prevent oxidation. It should then be cleaned as quickly as possible with a cotton swab soaked in carbon disulfide, benzene, chloroform, or ether, according to what is available and in the order of preference given here, ether being by far less effective than carbon disulfide. The affected area should then be observed carefully and cleaned again if the slightest trace of white fumes reappears upon exposure to air.

- Place powdered bismuth in a very small porcelain crucible. Add two or three drops of fuming HNO_3. The temperature rises rapidly while reddish-brown fumes are evolved. The heat generated is so great that the crucible may crack.

- Allow one drop of fuming HNO_3 to fall onto a few drops of aceton placed in a porcelain crucible or evaporating dish. An explosion occurs. Fortunately, it remains limited when the experiment is performed as described. This is a good reason never to store these two products in the same cabinet, especially when both are kept in glass bottles.

- In a porcelain dish, allow two or three drops of fuming HNO_3 to fall onto a very small quantity of formalin. A dangerous explosion occurs, accompanied by the evolution of NO_2. Here again, the effects remain limited because of the extremely small quantities employed. A fairly similar but even more spectacular experiment carried out with ordinary nitric acid will be described later.

Allow one drop of fuming HNO_3 to fall onto a few drops of an essential oil placed in a small dish. Ignition occurs.

- Allow a few drops of fuming HNO_3 to fall into a small quantity of methanol. Strong heating occurs and the alcohol may even ignite. Consequently, only a very small quantity of alcohol should be used.

- Allow a few drops of fuming HNO_3 to fall into a dish whose bottom has been covered with a layer of turpentine approximately 2 mm thick. Ignition occurs, accompanied by the evolution of black smoke consisting of fine carbon particles.

- Allow a few drops of fuming HNO_3 to fall onto salicylic acid. A red resin is obtained. Wash it thoroughly under running water and then boil it in a small quantity of water. After cooling, crystals of nitrosalicylic acid appear.

- Allow a few drops of fuming HNO_3 to fall onto a small quantity of pure aniline placed in a small dish. The reaction is very vigorous and may even be explosive (work behind a Plexiglas shield). A blue or green coloration is observed, rapidly turning red owing to the heat evolved. If a little water is added and the mixture is allowed to stand, a yellow coloration will be found together with a blue liquid at the bottom of the dish. Carbazotic acid has thus been obtained.
WARNING: The reaction with ordinary nitric acid is slower, but all the more treacherous and dangerous for that reason. After an induction period that may inspire false confidence, the reaction often starts suddenly and may become explosive. To carry it out, mix a small quantity of aniline with the acid and warm very gently while remaining protected behind a Plexiglas shield. A copious evolution of red fumes is observed and a yellow substance resembling sticky sulfur is formed.

- Allow a little fuming nitric acid to fall onto crystals of tartaric acid. Crystals of nitrotartaric acid are obtained. Dissolve them in water and heat to 40 °C. CO_2 is then

evolved and oxalic acid remains.

- The following experiment, however, may be carried out on larger quantities of materials.
Prepare separately, in three closed flasks, the equivalent by weight of one part sulfuric acid, two parts benzene, and two parts fuming nitric acid. While cooling vigorously with an ice-salt mixture and stirring by means of a suitable apparatus, slowly pour the sulfuric acid into the nitric acid. A yellow liquid is ultimately obtained which no longer gives off reddish-brown fumes. Then, while continuing vigorous cooling, add the benzene drop by drop to this mixture by means of a stopcock funnel. Each drop produces what appears to be a small explosion, and toxic reddish-brown fumes are again evolved. Ensure that the temperature never exceeds 4°C. Gradually, the liquid turns orange and then red after first assuming a milky yellow appearance. The entire liquid is then poured into a large separatory funnel filled with distilled water. Close it with a ground-glass stopper and invert it slowly before opening the stopcock to release the pressure and allow degassing. Shake the contents, which gradually become lemon-yellow. When the mixture appears homogeneous and no red portions remain, close the stopcock and return the funnel to its normal position in order to allow the contents to settle. Two layers are formed: a clear yellow upper layer and an opaque, oily, whitish-yellow lower layer. Collect the lower layer, which consists chiefly of mononitrobenzene (also rather inaccurately called oil of mirbane, since it has nothing in common with a true essential oil). This liquid is transferred to a fresh separatory funnel containing water to which ammonia has been added. Proceed as before in order to mix the two liquids thoroughly. Once again, two layers form, the lower one containing purer nitrobenzene.
Nitrobenzene is insoluble in water but soluble in ether, concentrated acetic acid, and sulfuric acid, with which it forms a reddish liquid. This substance is used in perfumery and for the manufacture of aniline.This experiment is such a classic that it is described in numerous manuals. It is nevertheless of limited value in an amateur laboratory, since it does not really lead to further complementary observations. If I have chosen to include it here, it is because the various authors who describe it often omit certain practical details, particularly the fact that if the benzene employed is not of laboratory-grade chemical purity, various dangerously explosive substances may be formed.

12.5 Simple Reactions with Organic Substances

Naphthalene

- Slowly pour picric acid into an alcoholic solution of naphthalene. A beautiful yellow crystalline precipitate forms.

- Pour concentrated HNO_3 onto solid naphthalene while stirring. A yellow liquid is obtained. Twenty-four hours later, the liquid has become more opaque and lemon-yellow in color. A similar result is obtained by placing a little naphthalene, a little manganese dioxide, and sulfuric acid in a flask.

- In a large test tube, place 2 or 3 cm of chloroform, then add a quantity of anhydrous aluminum chloride about the size of a pea. Mix, then add a little naphthalene. Mix again. A beautiful green deposit forms at the bottom and then turns blue. Stir again. It becomes green once more, then blue again. And so on... As the naphthalene dissolves, the amount of green/blue precipitate increases. In the end, the green precipitate is observed while stirring in front of a strong lamp.
Another way of carrying out this experiment is as follows: place naphthalene crystals, about half the size of a pea, in a test tube. Pour 2 cm of chloroform over them. Dissolve by shaking and make sure the walls of the tube are thoroughly wetted. Finally, dust the inside of the tube with anhydrous aluminum chloride, arranging things so that the powder comes into contact with the moist walls.
Gradually, a blue coloration appears wherever the powder and liquid have met. In fact, a trinaphthylmethane derivative is formed.
The same experiment may be performed using a little benzene instead of naphthalene. This time, however, the coloration is orange-red.

- In a small porcelain mortar, crush one naphthalene mothball, then add a slightly smaller quantity of powdered potassium chlorate and mix by simply stirring the mortar. Transfer this mixture to a 100–150 ml beaker and pour 2 cm of concentrated HCl over it. A vigorous reaction follows, with the evolution of abundant vapors. At the end, a reddish oily substance and a yellow solid remain.

Methanal or Formaldehyde or Formic Aldehyde (Formalin in aqueous solution)

- Prepare a small quantity of Fehling's solution of a sky-blue color in a test tube, then add a little formalin (35% aqueous formaldehyde solution). Nothing happens. Heat the mixture. The liquid changes from blue to green. Allow it to settle. A yellow layer deposits beneath a blue liquid. Decant most of this liquid and then add concentrated HNO_3. The precipitate disappears immediately and the liquid, now a beautiful blue, begins to foam.
WARNING: the reaction may suddenly accelerate and eject part of the liquid from the test tube because of contact between the acid and a portion of the formalin that has not reacted. To avoid this runaway reaction, the precipitate should be filtered and washed before being made to react with HNO_3.

- Cover the bottom of a beaker (standing in a large glass dish) with a layer of potassium permanganate about 1 mm thick, then pour 1 cm of formalin over it. After about one second, a violent reaction occurs. A black foam rises and often overflows from the vessel, running outside and transforming there into a black MnO_2 powder.

WARNING: This experiment is dangerous because a considerable quantity of formaldehyde is released. This gas is extremely toxic and irritates the eyes. It is therefore essential to carry out the experiment outdoors and with the wind blowing from behind the operator. This method, rarely mentioned in chemistry books, was formerly used to disinfect rooms thoroughly. It is still effective today but requires intense ventilation afterward. The use of goggles completely enclosing the eyes is strongly recommended.

- In a test tube 2 cm in diameter, pour formalin to a height of 2 cm. Then gradually add solid potassium hydroxide. Each addition produces vigorous effervescence and the liquid becomes warm. It eventually turns yellow. To be carried out outdoors!

Phenol

- Prepare a mixture of 6% potassium nitrite and H_2SO_4, then add phenol. Various color changes are obtained: brown, green, blue...

- An aqueous solution of phenol produces a brown or black precipitate in an aqueous or hydrochloric solution of gold salts.

- To phenol water containing a small amount of nitric acid, add concentrated sulfuric acid very slowly while stirring. The color changes from dirty yellow to orange and finally to a very dark red, eventually producing a precipitate.

- Add bromine water drop by drop to an aqueous solution of phenol. Each drop produces a white precipitate of tribromophenol, which then dissolves completely if ethyl alcohol is added to the liquid.

- Add a few drops of H_2SO_4 to about ten milliliters of phenol water and shake. Then add potassium nitrate crystals. A cherry-colored liquor is rapidly obtained, which then slowly changes into a dirty brown color. A strong pleasant odor can be detected.

- Freshly prepared nitrous acid is poured onto phenol. A red dye is obtained.

- In an Erlenmeyer flask, place one part of highly concentrated ammonia and four parts of water. Then add one part of bleach and finally one part of phenol water. The liquid turns green and then blue, especially if shaken. It is then allowed to stand and becomes transparent brown while releasing gas when shaken.

- Place a little potassium chlorate in a small beaker and pour concentrated HCl over it. When the yellowish vapors have ceased, add a little phenol. A new reaction occurs, this time with the evolution of red vapors. After standing, a yellowish-red substance is observed: perchloroquinone $C_{12}Cl_4O_4$, which has a greasy appearance when crushed between the fingers.

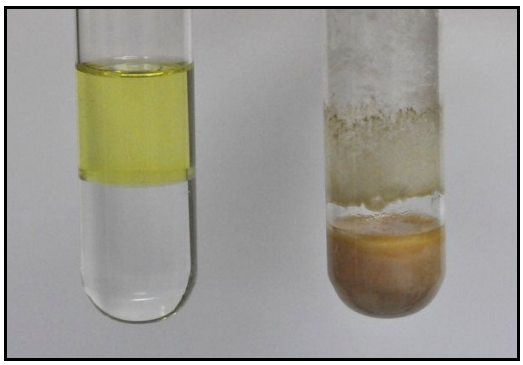


Figure 144

- In a large test tube, prepare a fairly concentrated solution of phenol in chloroform. Pour a concentrated KOH solution over it. Two immiscible layers form, the upper one becoming lemon-yellow within a few hours (Figure 144).
If potash is added in pellet form, the pellets become pink and then the entire liquid takes on this color while gradually turning more and more brown. This precipitate may solidify and then liquefy again. If this substance is divided into two portions and made to react respectively with water and concentrated sulfuric acid, the first gives a transparent liquid while the second produces a brownish-red liquid dye.

- A solution of phenol in ethyl alcohol poured into a pink aqueous solution of potassium permanganate colors it yellow-brown in less than one minute.

- Pour phenol water into an acid solution of mercuric nitrate. Very quickly, the liquid changes from colorless to a beautiful violet-red coloration which gradually turns brown.

- Prepare three test tubes containing phenol water. Add a few drops of an aqueous ferric chloride solution to each. The liquid becomes violet. Acetic acid is then added to the first test tube. The coloration disappears immediately. Glycerol is added to the second test tube. The color also disappears, but more slowly.
If a very small amount of lactic acid is added to the third the color changes to canary yellow.

- Place 30 ml of sodium hydroxide solution in a 100 ml ISO-type bottle and dissolve phenol in it. Stopper the bottle and place it in the freezer. When the liquid has solidified, warm it just to its melting point by shaking it between the hands, then add an excess of acetic anhydride. Shake. The temperature rises and two colorless layers form. A liquid is now present which causes abundant tearing when inhaled.

- Pour a little aqueous phenol solution into a test tube, then add a few drops of formalin or a little trioxymethylene (polymerized formaldehyde formerly used by veterinarians). Mix and then add concentrated H_2SO_4 drop by drop. Red clumps appear and, soon afterward, upon shaking, the entire mass becomes cherry-red before eventually turning brown

Resorcinol, Eosin and Fuchsin

- Place a spatula-tip quantity of resorcinol in a test tube. Add 2 cm of water and then a few drops of concentrated ammonia solution. Leave the test tube for one minute

in a fairly cool place. A slight yellow coloration appears. Heat very gently. The liquid turns orange. If heated further, it becomes very dark red, appearing black in a thin layer.

- Pour a little aqueous resorcinol solution into a test tube and add a few drops of formalin or powdered trioxymethylene. Finally, add concentrated H_2SO_4 drop by drop. Beautiful cherry-colored clumps are formed.
This experiment, as well as the previous one, refers back to what was said on pages 75-76 concerning the formaldehyde reagent for phenols.

- To an aqueous resorcinol solution, add drop by drop concentrated sulfuric acid containing a trace of nitric acid. A series of color changes is observed, ranging from yellow to red through orange, green, and even blue. The solution should be mixed after each drop. When the red color has been reached, adding an excess produces a red "mud."

- Prepare an aqueous solution of resorcinol and then very slowly add, while stirring, a strongly yellow aqueous ferric chloride solution. The original liquid gradually turns mauve and then yellow-brown.

- Prepare an aqueous solution of resorcinol slightly acidified with H_2SO_4 and divide it equally between two test tubes. In the first, add a potassium nitrate or sodium nitrate solution. The liquid takes on a yellowish tint. In the second, add a sodium nitrite solution. The liquid develops a goose-dropping-green coloration.

- Dissolve a spatula-tip quantity of resorcinol in 1 cm^3 of water and, separately, a spatula-tip quantity of potassium chlorate in 2 cm^3 of water. Place two or three drops of the chlorate solution in a test tube and then add 1 cm^3 of H_2SO_4. The liquid becomes yellow. Finally, allow two or three drops of the resorcinol solution to run down the side of the test tube. The color then changes from yellow to very dark green, eventually reaching violet-black.

- An aqueous solution of resorcinol reacts with limewater by becoming yellow and even greenish, but this is a slow reaction which does not become noticeable until after more than ten minutes.

- Prepare a solution of resorcinol in water and add a few drops of NaOH solution. The liquid becomes green. Then add a little chloroform and heat. The liquid becomes red.

- An aqueous solution of resorcinol to which a little ammonia has been added gradually develops a yellow-orange coloration and eventually a red one (depending on the concentrations), provided it remains in contact with air. The use of a paddle stirrer or a magnetic stirrer is useful here for accelerating the process.

-Prepare an aqueous solution of resorcinol and add bromine water drop by drop.

Each drop forms a yellow precipitate of tribromoresorcinol. Once the entire liquid is filled with this precipitate, add ethyl alcohol. The precipitate dissolves and forms a beautiful golden-yellow liquid.

-In a large test tube, place a fairly concentrated aqueous solution of a zinc salt, for example zinc sulfate. Gradually add ammonia while stirring. A white precipitate first forms and then gradually dissolves in an excess of reagent. Divide the liquid into two portions. To the first, add a little resorcinol solution in alcohol. It will be observed that the color of the liquid very gradually changes from very pale yellow to greenish, then to a definite green, and finally to blue. To the second test tube, also add the alcoholic resorcinol solution and then heat to a gentle boil. The color change is observed to occur more rapidly.
The same experiment may be attempted by replacing the alcoholic resorcinol solution with a solution of resorcinol in ether. In that case, the color change is slower.

- Place a quantity of sugar about one-quarter the size of a pea in a test tube and add a little water to dissolve it. Then pour in an alcoholic solution of thymol or resorcinol to a depth of 3 or 4 cm. Finally, allow H_2SO_4 to flow down the wall of the tube. Because of its high density, it will sink to the bottom and form a red-brown ring. The sugar may be replaced by pieces of filter paper. This is the Molisch test for carbohydrates. The color may vary from pink to violet. The test is very sensitive and therefore requires only a very small amount of sugar.

- Add nitric acid or hydrochloric acid to an aqueous solution of red eosin. In both cases, an orange flocculent precipitate forms, more rapidly and more intensely with hydrochloric acid. If ammonia is added instead, nothing happens. A sodium hydroxide solution, however, slowly modifies the color without producing a precipitate. The color becomes darker and darker until, after twenty-four hours, it gives the impression of a black liquid, violet or mauve by transmitted light under strong illumination.

- Prepare a pink aqueous solution of fuchsin. Add a little dilute ammonia. The liquid becomes colorless. Then add hydrochloric acid. The liquid turns yellow tending toward brown.

Camphor, Menthol and Thymol

- Take a long, narrow test tube (approximately 6 to 8 mm in diameter). Place a layer of camphor at least 2 cm deep in it and pour nitric acid over it without heating. The camphor appears to dissolve, but in reality a slightly yellow oil is formed. This is camphor nitrate. Allow the cloudy liquid to settle, then pour off the acid and add water. The camphor reforms, perfectly white.

- An early twentieth-century pharmaceutical book reported that a small amount of

iodine slowly imparts an indigo-blue color to menthol....
I therefore prepared an aqueous menthol solution to which I added a little iodine dissolved in a very small amount of potassium iodide solution. Only after several hours did I observe, in the test tube, the formation of a whitish-brown plug near the top, preventing the liquid from flowing out. After standing overnight, a kind of crystalline dendritic growth appeared along the upper walls of the test tube.

- A solution of thymol in alcohol develops a fleeting greenish color that rapidly changes from yellow to brown when ferric chloride is added. The ferric chloride must therefore be poured in very slowly.

- Place a fragment of thymol in concentrated acetic acid and wait until it has dissolved, at least partially. Then add a little sulfuric acid followed by a small amount of potassium nitrate. A green color then develops, followed by an ink-blue coloration.

Turpentine and Terpene Hydrate

- Allow concentrated H_2SO_4 to fall drop by drop into a small quantity of turpentine placed in a shallow dish. A brownish-red oily liquid first forms and gradually becomes homogeneous. Terebene is thus obtained.

- Drop a few iodine flakes into a small quantity of turpentine placed in a shallow dish. A slight ignition-like effect occurs and complex substances are formed, including a brown oil.

- Pour equal parts of turpentine and concentrated hydrochloric acid together. The two products do not mix, but a pink liquid quickly forms at the bottom and then becomes reddish-brown. It does not change over a period of fifteen days.

- Into 8 parts of turpentine, add 2 parts of ethyl alcohol and then 2 parts of HNO_3 while stirring continuously. This mixture is immediately poured into a crystallizing dish having a perfectly flat bottom and a sufficient diameter to ensure that the liquid layer remains fairly thin. It is important to add the three components in the order indicated here because of the danger involved in mixing alcohol and HNO_3 alone. During the following days, the liquid gradually turns brown and the odor of turpentine slowly disappears. Terpine crystals may appear around the third day.

- Pour concentrated sulfuric acid over terpene hydrate. An orange-red liquid appears. Then, with great care, add distilled water in small portions. After each addition and thorough mixing, a white liquid appears. Continue in this manner until the orange color has disappeared completely.

Oxalic Acid

- Pour freshly prepared hypochlorous acid onto oxalic acid. Chlorine and CO_2 are evolved and can easily be identified both by their odor and by bubbling them through baryta water.

- Introduce a mixture of oxalic acid and MnO_2 into a flask. Through a dropping funnel, add concentrated H_2SO_4 and collect the gas formed in limewater. The latter becomes cloudy because the gas is CO_2.

- If nitric acid is poured onto dry solid oxalic acid, a yellow to brown liquid is obtained. Heating is sometimes required to produce this result.

- Prepare a small quantity of lightly colored celestial water by mixing a dilute $CuSO_4$ solution with ammonia. Then add a little powdered oxalic acid. The coloration changes completely and becomes almost black.

- Place acetic anhydride in a ground-glass flask and then add oxalic acid crystals. Fit the flask with a stopper carrying a glass tube connected by flexible tubing to a Drechsel bottle containing limewater or baryta water. The reaction gradually begins in the cold and soon becomes significant. The limewater or baryta water turns cloudy, showing that CO_2 is being evolved. Remove the flexible tubing from the glass tube and, about one centimeter from its opening, once it is certain that the flask has been thoroughly purged of the air it originally contained, bring a lighted match close to it. A "blowtorch" is obtained, showing that large quantities of CO are also being evolved.

Tannin or Tannic Acid

- Add a tannin solution to a KOH solution. The liquid turns yellow and then becomes increasingly red as it absorbs oxygen.

- Add an alcoholic potash solution drop by drop to an alcoholic solution of tannin/tannic acid. A potassium tannate precipitate having a curious appearance is obtained and subsequently dissolves readily in water.

- Prepare an aqueous solution of tannin and add concentrated H_2SO_4. The liquid becomes brown. If this liquid is heated, it turns red and SO_2 is evolved.

- If concentrated H_2SO_4 is poured onto powdered tannin, a brown solid forms which becomes black when heated.

- Add a few drops of aqueous NaOH solution to an aqueous tannin solution. The liquid becomes orange to red. Then add ferric chloride solution. A blood-red to brown-black precipitate is obtained. Finally, if HCl is added, the precipitate

disappears.

- Prepare a pseudo-solution of calcium bicarbonate by passing an excess of CO_2 through limewater until the precipitate has completely disappeared. Then add a little tannic acid solution. Over the following hours, a precipitate reforms while a blue-green coloration appears as a ring in the upper part of the liquid. This ring is very visible after twenty-four hours. It forms as a result of an oxidation phenomenon. If, instead of leaving the liquid exposed to air in a wide-necked flask, air is immediately passed through it by means of a small pump, the precipitate reforms rapidly and, after about ten minutes, the air-agitated liquid already acquires a slight bluish coloration.

Picric Acid

- Add an aqueous solution of an alkali sulfide in excess to an aqueous solution of picric acid. Red picramic acid is obtained (heating afterward intensifies the color). This reaction is so sensitive that it can detect 1/5600 of picric acid.

- Add an aqueous sodium cyanide solution to an aqueous solution of picric acid. The liquid changes from yellow to a darker yellow. If heated, it becomes red.

- If picric acid is only very slightly diluted in NH_4OH and a sodium cyanide solution is added, a red coloration is likewise obtained, which gradually darkens, especially upon heating. This is also a sensitive reaction, detecting 1/4000 of picric acid.

- If celestial water is mixed with a picric acid solution, a yellow-green precipitate is obtained.

Pyrogallic Acid

AQUEOUS PYROGALLIC ACID SOLUTION

When a solution of pyrogallic acid is used, it must be prepared immediately before the experiment because it rapidly absorbs oxygen and does not keep.

- In a large test tube, place less than 2 mL of concentrated nitric acid and then add the tip of a lancetful of pyrogallic acid. The reaction is vigorous and produces a large amount of reddish nitrous fumes. Shake slightly and the mixture may even be warmed very gently. More nitrous fumes will be evolved. Blow a little air into the tube to decolorize it and then add a little water. The liquid is found to be yellow. Picric acid has in fact been formed.

- Prepare a dilute solution of chromic acid and pour it into a solution of pyrogallic acid. The color becomes reddish-brown owing to the formation of purpurogallin.

- If a solution of pyrogallic acid is poured into a solution of ferrous sulfate, an indigo-blue coloration is obtained without precipitation.

- If a solution of pyrogallic acid is poured into a solution of ferric chloride, the color changes from blue to reddish-brown without precipitation, depending on the concentration of the ferric salt.

- In a test tube, prepare a fairly dilute solution of potassium permanganate, then add a little pyrogallic acid and shake. The liquid becomes brown.

- If a solution of pyrogallic acid is poured onto limewater, a purple coloration is obtained without precipitation.

- If a solution of pyrogallic acid is poured into baryta water, a brown coloration appears and then turns black without precipitation.

- A solution consisting of a mixture of sodium acetate and ferric chloride, poured into a solution of pyrogallic acid, gives a magnificent blue-violet coloration.

- Into a solution of pyrogallic acid, allow a solution of iodine in chloroform to flow. Shake vigorously in the presence of air. The chloroform evaporates and the iodine combines to give a red coloration.

- In a narrow test tube, place about 2 cm^3 of a concentrated solution of pyrogallic acid, then add 2 cm^3 of a KOH solution and immediately stopper the tube with a finger before shaking. A red color appears. Open the tube under a water trough and the water rises because the oxygen of the air has dissolved in the liquid.

- Prepare a solution of pyrogallic acid and, separately, a dilute solution of sodium cyanide. Then mix the two. The liquid takes on a yellow to red color, depending on the concentrations. Allow it to stand. Slowly, the liquid loses its color except at the surface. Shake vigorously. The entire liquid becomes colored again. The operation may be repeated two or three times, but with decreasing success.

- In a test tube, place a solution of gold chloride and then add a very small amount of powdered pyrogallic acid. Immediately, the liquid, initially yellow, becomes brown.

- In a test tube, pour a moderately concentrated solution of pyrogallic acid. Add a little hydrochloric acid. Then add a 40% formaldehyde solution. A precipitate forms, first white, then rapidly pink, and finally fuchsia-colored.

Tartaric Acid

- To 2 cm^3 of a dilute freshly prepared tartaric acid solution, add a few drops of a 5% ammonium ferrous sulfate solution and a few drops of a NaOH solution. The liquid then takes on a green color. Add H_2O_2 and a brick-red coloration is obtained owing to a precipitate that slowly settles out.

Lactic Acid

- In a test tube, pour 3 cm of water, then add two drops of an $FeCl_2$ solution and two drops of HCl. The solution should then be slightly yellow. Add lactic acid. The yellow color becomes more intense.

- In a test tube, prepare a mixture of manganese dioxide and lactic acid. Then add sulfuric acid or hydrochloric acid and shake. After a while, the mixture begins to effervesce. Upon gentle heating, the reaction becomes more vigorous; the mixture foams more strongly and turns yellow, then brown, and finally black. Carbon dioxide is evolved and both a caramel-like odor and a formaldehyde odor can be detected.

- Into a test tube, pour a little concentrated chromic acid solution. Then, using a pipette, add lactic acid dropwise. The mixture foams vigorously and becomes completely black. It can easily be verified that carbon dioxide is evolved. Acetic acid is also formed.

Benzoic Acid

- A few drops of HCl added to a benzoic acid solution produce a fine white precipitate that is soluble in ether.

- Into a solution of ammonium or sodium benzoate, pour a little ferric chloride solution. A chamois-salmon colored precipitate of ferric benzoate is formed.
The same precipitate may be obtained in a somewhat more elaborate manner. To do this, first prepare a solution of benzoic acid in hot water (to increase the solubility of the acid). Then add an excess of ammonia to ensure complete neutralization of the acid and bring the solution to a boil to remove the NH_3. Allow it to cool and add ferric chloride. The precipitate obtained is quite different from the brick-red precipitate produced when ammonia is added to ferric chloride.

Salicylic Acid and Acetylsalicylic Acid

- To a solution of salicylic acid, add a few drops of ferric chloride solution. The liquid immediately turns violet. If a little mineral acid is added, this coloration disappears.

- An aqueous solution of salicylic acid to which a few drops of bromine water have been added forms a precipitate that is initially yellow and then rapidly becomes white.

- In two test tubes, prepare a mixture of sodium bicarbonate and acetylsalicylic acid, both dry. Add a little water to the first. The mixture begins to effervesce. Heat the second. A black, viscous product soon forms while an acetic odor is evolved.

Indigo and Indigo Carmine

- Prepare a not too dark solution of indigo carmine. Slowly add ammonia to it. The blue solution becomes green.

- Prepare an aqueous "solution" of indigo (in fact a mixture of water and insoluble indigo). Add a solution of potassium chlorate acidified with HCl. The indigo is decolorized.

- Pour concentrated HNO_3 onto a little indigo powder. The reaction is vigorous and reddish fumes are evolved. At the end of the experiment, a white powder remains.

Aniline

Aniline was and remains the basis of many synthetic dyes. The following experiments make it possible to obtain a number of simple dyes from it.

- In a test tube, place a few drops of concentrated HNO_3 and then a spatula-tip of potassium chlorate. Shake and then add a drop of aniline. A strong blue coloration is obtained. Attention: if the order of addition is reversed by placing the aniline first, then the acid, and finally the chlorate, and if larger quantities are used, a violent reaction accompanied by a flame may occur. In the latter case, a kind of black precipitate is obtained which dissolves in amyl alcohol.

- To a few drops of aniline add 1 mL of H_2O_2 and 1 mL of H_2SO_4 and then, slowly, a solution of a chlorate. If a blue coloration does not appear immediately, add a little more H_2SO_4.

- In a beaker, prepare a mixture of an aqueous solution of potassium ferricyanide and hydrochloric acid. Then add the aniline dropwise. The first drops seem to disappear into the mixture while leaving a slight trail of fumes behind them. Afterwards, each drop causes the appearance of green spots which soon turn blue.

- Pour sulfochromic mixture onto a small quantity of aniline. A very red precipitate is obtained, followed by violet and then blue colors.

- Mix an aqueous solution of chromic anhydride with aniline. Depending on the concentration of the solution, a liquid is obtained whose color varies from goose-green to dirty brown or even black.

- In a large test tube, pour about 2 cm of acetic anhydride. Carefully add about 0.5 cm of aniline and mix slightly. A very considerable evolution of heat occurs and the entire liquid takes on a brownish-red coloration. When the liquid has cooled, the odor of the anhydride can still be perceived. Add another quantity of aniline. The same result is obtained. Continue adding aniline as many times as necessary until, after the considerable heating of the material, the mixture solidifies completely on cooling into a reddish crystalline mass of acetanilide, which is used in the manufacture of many medicines.

- To about 3 cm^3 of aniline, add a concentrated solution of potassium dichromate. Shake vigorously and for a prolonged period. Black, immiscible globules are formed. This is a coloring substance known as aniline black.
The experiment may also be carried out with a little aniline mixed with a few drops of H_2SO_4. A white precipitate first forms and then disappears when a dilute dichromate solution is added. Instead of black globules, a kind of very black ink is obtained.

- First prepare a little aniline water by placing a few drops of aniline in water and shaking vigorously. Then pour 2 cm of sodium hypochlorite solution (bleach) into a large test tube. Add two drops of aniline water and mix, first slowly and then more rapidly. A red coloration soon developing into mauve-violet appears. Then carefully pour ethyl alcohol on top. An immediate goose-green coloration is obtained. If a dilute bleach solution and only a small amount of aniline water are used initially, the violet and green colors are more pronounced. The green, however, tends toward yellow after about ten minutes. If, before adding the aniline, 2 cm^3 of a NaOH solution are added in order to make the bleach strongly alkaline, the coloration obtained with aniline is ruby-red and then becomes blue upon addition of ethyl alcohol. The same experiment carried out with chlorine water gives a mauve-violet coloration with aniline water and this no longer changes after the addition of alcohol.

- Add a few drops of aniline to a small quantity of sodium hypochlorite solution (bleach). A brick-red precipitate is obtained which rapidly changes into oily blue-black droplets. If the order of addition is reversed and bleach is poured into the aniline, a blue coloration is obtained immediately.

- In a test tube, place a few drops of concentrated nitric acid, then a few drops of a sodium nitrite solution and finally one or two drops of aniline. After slight agitation (a faint white cloud may form), add a little sodium hypochlorite solution. A blue or green coloration is obtained.

- If a mixture of aniline water and phenol solution is prepared and a little NaOH is

added, the addition of hypochlorite produces a very dark blue precipitate which, when heated, gives an ink-blue liquid.

- Into a concentrated copper sulfate solution, pour some aniline. A green precipitate is formed.

- Into a solution of sodium hypobromite prepared immediately before the experiment, add a little aniline. An orange precipitate is obtained which may range to red (Kermes red).

- Pour freshly prepared nitrous acid onto a small quantity of aniline. A red dye is obtained.

- In a large test tube, pour a layer about 3 cm high of a sodium nitrite solution and, above it, add a few drops of aniline. Shake vigorously to obtain a grayish-yellow emulsion. Then dip a thin glass stirring rod into sulfuric acid and, after allowing it to drain, use it to stir the emulsion. This slight acidification is sufficient to initiate a reaction: a beautiful sunflower-yellow liquid is obtained, above which float small droplets of unreacted aniline.

- In a test tube, place a few drops of concentrated nitric acid, then a few drops of a sodium nitrite solution and finally one or two drops of aniline. A red coloration is obtained, especially upon warming.

- Pour bromine water onto a few drops of aniline placed in a test tube. A milky precipitate first appears and rapidly becomes lighter in color. Tribromoaniline has been formed.

- Onto a small quantity of aniline in a test tube, pour a hydrochloric stannous chloride solution. A white precipitate resembling a plastic layer is obtained. It can be dissolved in HCl.

- To an aqueous solution of aniline obtained by gentle heating, add a little formaldehyde solution. A white precipitate of anhydroformaldehyde aniline is obtained.

Hydroquinone

- Hydroquinone, which occurs as soft flakes, was once widely used for developing photographic prints. After having long been employed by dermatologists, it was later extensively used by dark-skinned individuals wishing to lighten their skin through its action on melanin. This misuse led to the substance being banned from all cosmetic products, and it has now become difficult to obtain. It is a very powerful reducing agent capable of producing a series of interesting experiments. All those described below should be carried out with a fairly concentrated aqueous solution.

- To the concentrated solution made alkaline by the addition of a little sodium bicarbonate, add dropwise a solution of iodine in water containing KI. With each drop added, the iodine that forms immediately disappears upon agitation, while the solution gradually takes on an increasingly yellow color.

- Into the concentrated solution, add an aqueous solution of potassium permanganate drop by drop. Each drop is instantly decolorized upon agitation while the solution gradually turns yellow.

- Add drops of ferric chloride to the concentrated solution. Each produces a green streak of ferrous salt which then disappears while the solution gradually becomes yellow. A test carried out with potassium thiocyanate shows that the precipitate now obtained is not the same as that which would be produced with a ferric salt.

- To the concentrated solution, add a little aqueous potassium chromate solution and then one or two drops of sulfuric acid. Here again, striking color changes are obtained.

- To the concentrated solution, add a little aqueous silver nitrate solution. A gray turbidity slowly appears and gradually develops into a precipitate that becomes darker and darker until it is black.

- To the concentrated solution, add a little cupric acetate. The liquid becomes golden yellow. If a little HCl is then added, an emerald-green color is obtained. If, on the other hand, the golden-yellow solution is heated, a brick-red cuprous oxide solution is obtained together with a yellow stain on the wall of the test tube.

- This time, dissolve a small quantity of hydroquinone in 3 to 4 cm^3 of alcohol and then add a NaOH solution. The previously colorless liquid immediately turns orange.

Albumin (Egg White)

- Mix egg white with a mixture of 1 volume of H_2SO_4 and 2 volumes of acetic acid. A red coloration is obtained.

- To egg white, add 1 cm^3 of a 10% aqueous KOH solution. Then add dropwise a 1% $CuSO_4$ solution. A red coloration is obtained.

- Pour a mercuric nitrite or mercuric nitrate solution onto egg white. A white precipitate is obtained which becomes red upon heating.

Thymol

- See the Molisch test described above with resorcinol.

- In a test tube, place an amount of thymol crystals about the size of a quarter of a pea and dissolve it in approximately 20 mL of water, warming gently if necessary. Then add a little ammonia and finally a little bleach (sodium hypochlorite solution). Upon addition of the bleach, the liquid becomes yellow. On shaking, it changes color, becoming green and then blue. If allowed to stand, the color may return to yellow. It is then sufficient to shake again for it to revert to green-blue. If this liquid is heated, it becomes much darker and then, when left at rest, takes on a cherry-red shade while giving off a pleasant resinous odor.

- In a test tube, dissolve a little thymol in a NaOH solution. Then add this solution very gradually to a relatively concentrated aqueous solution of iodine and potassium iodide. A reddish-brown precipitate of iodothymol is formed. This substance is soluble in ether, chloroform, and carbon disulfide. Attention: if too much of the thymol-NaOH solution is added, iodothymol does not form and the liquid rapidly becomes colorless.

- In a porcelain mortar, grind a little thymol with sodium hydroxide and then pour a little chloroform over the mixture. A violet solution is obtained.

- Dissolve a small crystal of thymol in hot water and then slowly add a solution of $FeCl_3$. A cloudy olive-colored liquid is obtained which, upon heating, becomes distinctly raw sienna in color and completely turbid.

- Dissolve less than one gram of thymol in one cubic centimeter of glacial acetic acid and add three drops of H_2SO_4 followed by one drop of HNO_3. The liquid immediately becomes duck-blue. With time, it changes to orange while the test tube fills with NO_2.

- A dilute aqueous solution of thymol prepared hot gives a milky turbidity when formaldehyde solution is added. This turbidity later settles into yellowish oily droplets.

Other Organic Substances

- In a bottle, place carbon tetrachloride, a piece of zinc, and a little hydrochloric acid. Close with a cotton plug or a porous stopper. Mix regularly so that the acid comes into contact with the zinc. The nascent hydrogen evolved soon causes the appearance of a yellowish liquid floating on the surface. It consists of impure chloroform.

- In a bottle closed with a stopper that is only partially screwed down, place one-third aceton, one-third carbon disulfide, and one-third concentrated ammonia. Shaking is unnecessary. Two layers rapidly form, one milky and the other pink. The pink layer then becomes increasingly orange-red while a third layer of the same color appears. After 24 hours, oily droplets have formed and yellow crystals of a

complex hydrogensulfide appear.

- Add sulfochromic mixture dropwise to aceton. An orange precipitate forms and adheres to the walls of the bottle when shaken. After standing, this precipitate becomes dark brown to black and settles to the bottom of the bottle.

Prepare an equal-parts mixture of concentrated H_2SO_4 and concentrated HNO_3 and allow it to cool. Pour it into a long test tube held vertically. Then, using a pipette, add a little isopropyl alcohol. A strong evolution of red and then colorless gases occurs, after which the reaction, initially tumultuous, gradually subsides (Figure 145).

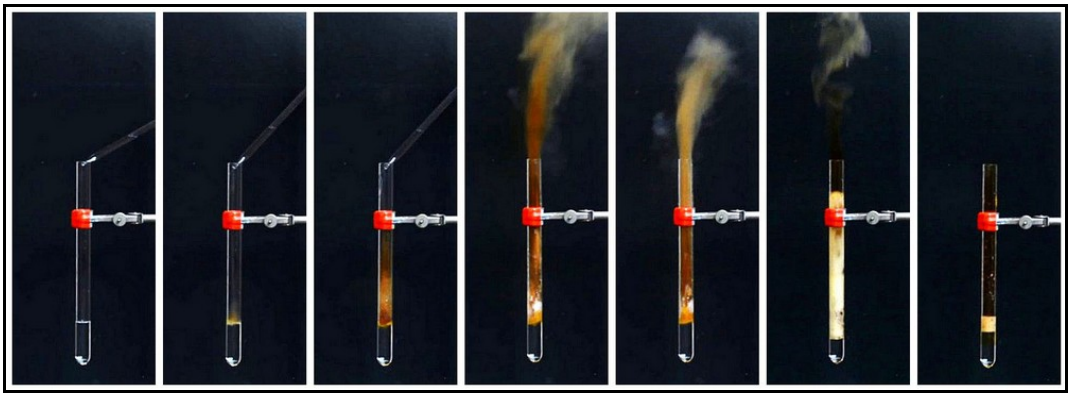


Figure 145

- Here is an experiment that is simple in its execution but whose reaction is complex. Place a 300 mL two-neck flask in an ice-water bath on a magnetic stirrer. Pour into it approximately 200 mL of a mixture consisting of equal parts isopropyl alcohol and a very concentrated aqueous sodium nitrite solution. Start the stirring and allow the liquid to cool thoroughly. Then leave one neck open and, through the second neck fitted with a dropping funnel, slowly add 50 to 75 mL of a concentrated aqueous solution of aluminum sulfate. The aluminum nitrite undergoes complete hydrolysis and nitrous acid (HNO_2) together with aluminum hydroxide are formed, the latter giving the liquid in the flask a milky-white appearance. When the funnel is empty, continue stirring for two minutes and then transfer the liquid from the flask to a stoppered separatory funnel. Slow settling reveals at the surface a yellow liquid consisting of isopropyl nitrite. The nitrous acid has indeed esterified the isopropyl alcohol. Isopropyl nitrite was the principal constituent of the famous poppers that were so popular in the gay community during the 1980s.

- Prepare a concentrated aqueous solution of sodium potassium tartrate. Gradually add acetic acid. A white crystalline precipitate forms and dissolves in ammonia.

- Prepare a concentrated urea solution. Slowly add concentrated HNO_3. Depending on the concentration, it may be necessary to shake for some time before a white precipitate of urea nitrate forms. Depending on the concentration, evolution of CO_2 may also sometimes be observed. The urea nitrate obtained is white and sparingly soluble in cold water and alcohol, but soluble in boiling water.

- A potassium dichromate solution acidified with H_2SO_4 reacts with urea, producing CO_2 (easily detected) but also nitrogen, which an amateur chemist cannot readily detect.

- In a large test tube, place a saturated glucose solution. Then prepare a permanganate solution containing a weight of permanganate equal to that of the glucose used. Since permanganate is not highly soluble in water, it is advisable not to start with too large an amount of glucose. Pour the second solution into the first while shaking vigorously. The temperature rises and manganese dioxide forms, either slowly or rapidly depending on the quantities used, eventually setting into a gelatinous mass.

- Fill one-third of a 3–4 cm diameter footed, ungraduated test tube with fairly fluid tomato juice. Slowly pour over it one-third of a well-concentrated bromine water solution. Stir slowly throughout the entire height of the liquid, either by rotating a glass rod along the wall of the tube or by using a magnetic stirrer. Various colors gradually appear, ranging from blue to yellow through green. Eventually, after some time, the liquid becomes completely yellowish-green (Figure 146).

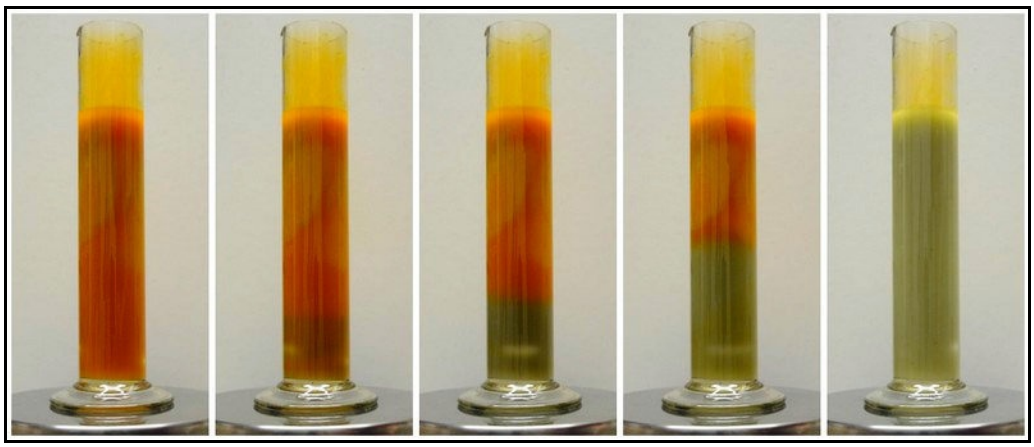


Figure 146

- Into a test tube containing a little terpin hydrate, slowly pour concentrated H_2SO_4 while stirring. A fairly viscous red liquid is obtained. If this liquid is then poured into another test tube containing five or six times as much water, a white resinous substance precipitates. This substance dissolves in ethyl acetate, which is sometimes required for cleaning the test tube.
Repeat the same experiment, that is, pour concentrated sulfuric acid onto terpin hydrate; then this time add a little vanilla sugar. A violet coloration is obtained owing to the reaction of vanillin (artificial vanilla).

- To an aqueous quinine sulfate solution, add chlorine water and then ammonia. A beautiful transparent liquid is obtained, emerald-green or duck-blue depending on the concentrations. This coloration remains stable over time.

- To a very dilute quinine sulfate solution, add three or four drops of bromine water

until the liquid becomes pale yellow. Then gradually add an excess of ammonia. The liquid takes on a shade varying between blue and green, depending on the concentrations.

- To an aqueous quinine sulfate solution, add a little baryta water. A milky precipitate forms immediately and disappears at once upon addition of chlorine water.

- In a test tube, place two or three centimeters of water and a pinch of gum arabic, then shake vigorously. A yellowish, lumpy-looking liquid is obtained, coating even the walls of the entire test tube. Add a little HCl. Immediately, as the acid reacts with the gum arabic salts, the liquid becomes clear while remaining yellowish. Then add a substantial quantity of ethyl alcohol and shake. The entire liquid turns white because arabin is precipitated. Being very light, it eventually floats on the surface of the liquid.

- Pour a little whole milk into a bottle. Then slowly add vinegar and shake. The liquid gradually becomes curdled and deposits a white solid consisting of casein.

- Mix cotton with a fairly concentrated NaOH solution. The cotton turns yellow and becomes pasty. A compound known as alkali cellulose is thus obtained. When placed in a closed vessel with CS_2 and shaken periodically, this compound hardens while oily droplets adhere to the walls of the bottle. After a few days, it can be observed that this substance reacts very violently with nitric acid. The bottle should then be emptied, rinsed with aceton and finally with concentrated nitric acid, after which it may be washed normally.

- Place a drop of somewhat diluted nitric acid on the palm of the hand or on a finger. Wait no more than one second before rinsing immediately with plently of water and then again with sodium bicarbonate solution. By the following day, a clearly visible yellow stain appears, especially noticeable on a fair-skinned person. Later, the stain hardens and finally a layer of dead skin peels away in large flakes while new skin appears underneath. The yellow color of the skin is due to the formation of picric acid. This experiment obviously requires caution and experience.

- Hard waters (containing calcium salts) were once unsuitable for washing clothes because they prevented soaps from lathering. To detect them, a few drops of an alcoholic solution of Marseille soap were used; with hard water, a white precipitate formed. The addition of sodium carbonate to hard water, however, allowed the soap to lather and thus made the water suitable for washing clothes. These tests can easily be repeated. The use of modern detergents has eliminated this problem... while creating other well-known ones (among them the proliferation of green algae).

- Prepare an aqueous solution of Marseille soap and add either an aqueous ferric chloride solution or concentrated HCl. In both cases, the formation of a precipitate is observed.

- Methylene blue dissolves in concentrated H_2SO_4 to give a green liquid. When poured into water, this liquid becomes blue.

- In a test tube, place a sodium hydroxide solution to which one drop of phenolphthalein has been added. Add a piece of zinc. The nascent hydrogen rapidly decolorizes the solution. This reaction is used in the Kastle–Meyer blood test.

- In a test tube containing 2 cm^3 of concentrated H_2SO_4, add two drops of lavender oil and shake. The entire liquid immediately takes on a beautiful red coloration.

Chlorophyll and Colored Flowers

- A fairly classic experiment combining chemistry and biology consists of extracting chlorophyll from green leaves by macerating them in ethyl alcohol. To facilitate grinding with the pestle, a quantity of fine washed sand is added to the mortar. The emerald-green liquid thus obtained is then filtered. It can be shown that this liquid contains several coloring substances by carrying out a simple chromatography using a long strip of filter paper, only the end of which is immersed in the liquid. Several bands then appear along the strip. Another way of demonstrating this consists of mixing the green liquid with dilute hydrochloric acid, then adding ether and shaking. In principle, two layers form: a blue one below and a yellow one above. However, the experiment is difficult to perform and it is sometimes necessary to repeat it several times before obtaining the two colored layers. Proceeding in reverse order is sometimes advisable, that is, first pouring in the ether, mixing, and then gradually adding the acid.
A final method gives a more obvious result. Baryta water is added drop by drop to the original green liquid. A light, dark-green flocculent precipitate forms. It is insoluble in alcohol and very gradually settles to the bottom of the test tube, while the alcohol, deprived of the substance that has reacted, takes on the yellow color of the other principal substance. Illustrations 147 and 148 show various results obtained by these different methods.

Figure 147

Figure 148

- Interesting and amusing experiments can be carried out with colored flowers. They were studied at length by the chemist Filhol. It had long been known that SO_2 gas or its aqueous solution (H_2SO_3) had the property of instantly bleaching certain flowers which, once exposed again to air, sometimes gradually regained their original color. Filhol used ether mixed with a little ammonia and observed that many red, pink, or violet flowers instantly turned green when immersed in this mixture. Yellow flowers, on the other hand, were not altered. The Italian Gabba carried out other experiments using simply ammonia vapors or hydrochloric acid vapors. He thus obtained numerous color changes and even modifications of fragrance. Gabba also reported changes in flower coloration when they were touched with nitric acid. There are so many possibilities here that each reader should be left to experiment and discover with a sense of wonder, for these are entirely safe experiments (there is indeed no danger that a flower will explode!).

- Fill a flask with rose petals (red or pink) and pour alcohol over them. Stir and allow the mixture to macerate for one or two hours, shaking from time to time. The petals quickly lose their color and the liquid becomes yellowish. Filter it. If a few drops of an acid are added to this liquid, it turns pink. If a few drops of ammonia or a NaOH or KOH solution are added, it turns green and gradually blue-green. The same occurs with limewater or baryta water. It is preferable to use dilute acidic or basic solutions. With a more concentrated caustic soda solution added dropwise, several different superposed shades may be obtained, formed by various precipitates. Other flowers provide similar reactions, starting from alcoholic solutions having different initial colors.

- An alcoholic extract of red tree leaves appears green in the light of a fluorescent tube and in sunlight, but red in the light of an LED lamp.

12.6 Some Unusual Experiments

- In a flask that can be closed with a screw cap, prepare aqua regia. Once it has acquired a golden-yellow color, add carbon disulfide and close the flask incompletely with the screw cap so that gases can escape. Shake periodically and allow the flask to stand in a cool place. The liquid gradually turns blood-red while insoluble red globules accumulate at the bottom.

- Place approximately three centimeters of ethyl alcohol in a test tube, followed by 5 mm of carbon disulfide. Finally, add a pea-sized quantity of solid NaOH and shake. The liquid warms up and rapidly becomes canary yellow. Sodium xanthogenate has been formed. If an aqueous copper sulfate solution is added to this yellow liquid, a precipitate is produced whose color may vary, depending on concentrations, from canary yellow to brownish yellow.
If an aqueous molybdic acid solution is added to the same yellow solution, a pink precipitate forms and gradually becomes mauve before settling to the bottom of the

test tube.

- Here is an experiment that cannot fail to intrigue. Begin by preparing a concentrated aqueous solution of boric acid. This must be done several hours in advance, with regular shaking of the flask. At the same time, prepare a 50% aqueous glycerin solution. When ready to begin the experiment, add a few drops of phenolphthalein to each flask and observe that both liquids remain colorless. Then add a few drops of NaOH solution to the glycerin flask in order to produce a strong coloration of the indicator, and gradually add the same NaOH solution to the boric acid solution until it reaches the same color as the glycerin solution. Two distinctly alkaline solutions are now present. Mix them together and observe that the resulting liquid becomes completely colorless once again. At each stage, carefully measure the pH of the solutions. The result may come as a surprise. In fact, mixing these two alkaline solutions forms an acid formerly known as boroglyceric acid.

- In a 250 mL flask that can be tightly stoppered, place one-third water, two teaspoonfuls of calcium hydroxide, and a layer of carbon disulfide about half a centimeter deep. Stopper the flask and place it on a magnetic stirrer operating at more than one thousand revolutions per minute for several minutes. Then allow it to stand for 24 hours. The liquid becomes pink and then increasingly orange while the odor of carbon disulfide decreases markedly. If a little of the orange liquid is removed and heated, it leaves an orange solid residue.

- Measure very accurately a given quantity of absolute alcohol and the same quantity of water. The two liquids are then poured into a volumetric flask whose calibration mark corresponds to the arithmetic sum of the two measured volumes. It will be observed that the mixture does not reach the calibration mark, and it must therefore be concluded that a contraction of the total liquid volume has occurred. One should therefore beware of certain preconceived ideas: the total volume occupied by two mixed liquids is not necessarily equal to the mathematical sum of their original volumes. How many people know this?
The same type of experiment may be carried out by pouring a volume of concentrated sulfuric acid into an equal volume of water and observing, in addition, the considerable heat evolved by the operation.
One may even imagine a pedagogical game based on the equation 1 + 1 = 2 or 1,...?

- Prepare a saturated NaCl solution in water and fill two test tubes to two-thirds of their height. Pour alcohol into the first and concentrated HCl into the second. In both cases, NaCl precipitates from solution. Shake each test tube thoroughly. In the HCl tube the crystals are fairly large and settle rapidly. In the other they are very fine and settle slowly.
Here is a way to produce a sequence of major changes in the appearance of a liquid. Such an experiment, both amusing and intriguing, can serve perfectly as an introduction to a chemistry lesson.

- Prepare a sodium carbonate solution and pour 3 to 4 cm of it into a long, wide test

tube or into a long tube closed at one end with a stopper. Then add the following solutions successively, continuing each addition until a clearly visible precipitate forms or disappears:
silver nitrate → brown color
sodium hydroxide → black
sodium chloride → white (avoid leaving it exposed to light for too long)
ammonia (not too concentrated) → the solution becomes clear
sodium bromide → new whitish-yellow precipitate
sodium thiosulfate → the solution becomes clear again
sodium iodide → new yellow precipitate
sodium sulfide → black precipitate

- Here is an experiment that may explain one method used in dyeing fabrics. The principle is to color cotton or wool by forming precipitates within the fibers themselves. It may also be shown that this does not work with synthetic fibers.
Take three beakers. Place dilute acetic acid in the first, a ferrous sulfate or ferrous chloride solution in the second, and a potassium ferrocyanide solution in the third. Dip a square of white cloth into the first beaker, then into the second, and finally into the third. The cloth emerges with a beautiful blue color (Prussian blue). Allow it to dry.
Take two beakers. Place a strongly acidified lead acetate solution in the first and a potassium dichromate solution in the second. Dip a square of white cloth into the first and then into the second. It emerges from the second beaker with a bright yellow coloration. Allow it to dry. These colors remain stable over time (Figure 149).

Figure 149

- Here is how to transform filter paper. Immerse a square of filter paper for 5 to 10 seconds in concentrated H_2SO_4 and then place it in a small beaker containing aqueous ammonia. Remove it and allow it to dry. Once dry, the filter paper will have been transformed into parchment paper. If, upon removal from the H_2SO_4, the paper is immersed in pure water, it is immediately destroyed by carbonization.

- In a plastic container that can afterwards be discarded (for example, a small PVC bottle cut open for the purpose), place 40 mL of sodium silicate solution. Then add 10 mL of ethanol. Shake rapidly while stirring with a glass rod. A complex white gel soon forms and adheres to the glass. Wearing latex gloves, remove the gel from the glass rod and squeeze it. Then roll it between the hands to give it the shape of a ball. This ball will bounce strongly when dropped onto the floor. Gradually, however, it will continue to release ethanol, especially if slightly compressed, and it will harden slowly. Care should be taken not to bring it into contact with glass. It is better to leave it resting on absorbent paper, reshaping it from time to time to prevent it from flattening. It will eventually become completely hard, but it will not remain compact.

- Many experiments are exothermic in nature, that is to say, they produce a more or less considerable evolution of heat. Others, less common, are endothermic, meaning that they absorb heat and therefore appear to produce cold. If ether is poured onto the hand, the liquid absorbs the heat required for its evaporation and therefore produces a sensation of cold. Some substances lower the temperature simply by dissolving. Ammonium chloride, for example, does so when dissolved in water. Certain mixtures produce a very considerable drop in temperature, such as crushed ice mixed with calcium chloride (see Addendum 5). A reduction in temperature may also be obtained by intimately mixing, in the dry state, 5 parts of barium hydroxide with 2 parts of ammonium thiocyanate and then spraying a little water onto the mixture. The same applies to barium hydroxide and ammonium nitrate. By using sufficiently large quantities of these reagents, it is even possible to freeze a thin layer of water placed between the reaction vessel (if it has a flat bottom) and, for example, a light plastic sheet. The two surfaces will then become frozen together.

- Here is a curious experiment. In a small porcelain vessel, mix a little natural camphor with menthol. Using a small glass or porcelain pestle, grind the two substances together. Very quickly, these solid materials liquefy and form a kind of oily gel. This new substance may possess certain medicinal properties. It should not, however, be used without serious medical advice.

12.7 Spectacular Reactions

From a psychological and educational point of view, it is clear that a spectacular chemical reaction is more likely than an ordinary one to capture the attention of students and facilitate its retention in memory. It may even inspire enthusiasm for the study of chemistry. The following experiments belong to that category and are easy to perform. Before discussing them, however, allow me to say a few words about one of them, perhaps the most famous of all from a literary point of view.

The experiment known as Lémery's Volcano has often been described as spectacular in numerous chemistry treatises and even in popular science books. Authors who presented it as a classic and frequently performed experiment generally contented themselves with stating that a moist mixture of iron powder and sulfur gathered into a heap heats spontaneously until the whole mass suddenly combines, ejecting a considerable amount of material and water vapor, somewhat like a volcano. Some authors were only slightly more precise, adding that the water poured onto the mixture of iron and sulfur should initially be hot. L. Houllevigue, in L'Évolution des Sciences (Paris, 1855), explained that Lémery (1645–1715) had in some way attempted to understand and explain volcanic phenomena by burying the famous mixture, which then behaved like a genuine volcano. B. Bourdoncle, in Dix-sept Histoires de la Chimie (Paris, 2003), asserted that in order to succeed, Lémery had to throw a live ember onto the top of the buried mixture. Yet all of this is partly or entirely false, because it is more than likely that none of these authors ever

attempted to reproduce Lémery's experiment or, if they did, were too embarrassed to admit that they had failed. The certain fact is that, had they succeeded, they would undoubtedly have specified the exceptional conditions required for its realization. It was probably by consulting primary sources that G. Francis, in his book Chemical Experiments (several editions published around 1845), was able to describe in detail the experiment that the chemist Lémery performed in order to astonish those he wished to interest in chemistry. He used nearly 13 kg of sulfur and 13 kg of iron (28 imperial pounds of each constituent, the pound corresponding to approximately 453 g), mixed them with hot water to form a homogeneous paste, and buried the mass at a depth of 60 cm in the ground where the reaction began. Only after 12 to 14 hours did the soil become lifted by jets of yellowish ash. G. Francis emphasized the importance of burying the mass so that the heat could be retained as effectively as possible and added that it was not prudent to remain nearby after ten hours had elapsed.
This clearly shows how greatly historical reality differed from the theoretical descriptions proposed by many authors who did not take the trouble either to consult primary documents or to attempt the experiment themselves.
In truth, the combination of iron and sulfur can be carried out more or less as many authors describe, but it is then not spectacular in the least. Take two equal parts by weight of flowers of sulfur and iron powder. The iron must first be washed with ether and then with HCl in order to remove every trace of grease and rust. Once all traces of acid have been removed by washing with water, it is mixed with the sulfur and a small quantity of hot water to form a thick paste. This paste is then packed into a flask closed with a stopper pierced by a small hole and wrapped in aluminum foil in order to prevent the dissipation of heat. The reaction then proceeds gradually, the material agglomerating into a solid block while a rotten-egg odor becomes noticeable

- Another well-known laboratory "volcano" is obtained from solid ammonium dichromate arranged in the form of a small cone. Simply ignite the tip of the cone with a match. The combustion spreads in all directions, producing glowing sparks while nitrogen is evolved. At the end of the reaction, a fine powder of chromium sesquioxide remains, occupying a volume far greater than that of the original cone.

Figure 150

- Here is, in a sense, a liquid volcano. Take a 100 mL beaker and pour into it slightly less than one centimeter of commercial nitric acid. Then carefully add about the same quantity of 90–95% ethyl alcohol and move away quickly. Gradually, sharp cracking noises are heard, accompanied by the evolution of gases. The entire beaker is shaken by the reaction. Finally, the crackling becomes more frequent and more rapid, and red nitrous fumes rise from the vessel in which the liquid suddenly appears to erupt, throwing projections in all directions (Figure 150).
WARNING: Wait until the reaction has completely subsided and flood the vessel with

water from a distance before recovering it. This experiment must be carried out outdoors, on a concrete surface that is not affected by staining, and NEVER with fuming nitric acid. Always use a wide-mouthed vessel such as a beaker, and under no circumstances approach it during the reaction.

TWO VERY USEFUL PROTECTIVE DEVICES

It may happen that certain reactions produce projections in all directions.

A first valuable protective device in such cases can easily be obtained from a glazier. Simply ask for a small square glass plate with a circular hole 2 to 3 cm in diameter drilled through its center, allowing liquids to be poured or solids to be introduced. This plate can be placed over a beaker-type vessel to cover it. It will already stop a considerable number of projections that might emerge from the vessel.

A second protective device can easily be constructed. Simply purchase a transparent Plexiglas sheet from a hardware store and provide it with "feet" by attaching metal brackets to its base. This movable shield should first be cut to whatever size appears most suitable, allowing the operator to pass his or her arms comfortably around either side while performing a manipulation. Such a shield may also be mounted on hinges fixed to the ceiling so that it can be lowered between the experimenter and the laboratory bench during, or before, an experiment.
Warning: This protective screen should never be placed too close to a strong source of heat or to an open flame.

- Place a few KOH pellets in a test tube and then add glacial acetic acid. At first nothing happens, but after a while small explosions are heard and, occasionally, projections occur. The reaction is rather unpredictable and therefore requires caution at every stage.

- In a small 100 mL ground-glass Erlenmeyer flask, a tightly closing medicine bottle, or even a stoppered test tube, dissolve as much sodium acetate as possible while heating. Do not be surprised: a large quantity of sodium acetate is required. Once the solution is fully saturated, stopper the vessel and allow it to cool away from shocks and vibrations. When the flask has become completely cold, drop a small fragment of sodium acetate into it or touch the liquid with a copper rod. The entire liquid then solidifies, the reaction propagating steadily throughout the mass and producing considerable heat. This experiment may be repeated by reheating the flask and, if necessary, adding a little water followed by more sodium acetate. In teaching, such a flask may be kept and reused every year, thus avoiding waste of sodium acetate.

- Take deliquescent copper nitrate and sprinkle a little magnesium powder onto it. A sort of small explosion occurs and red nitrous fumes are evolved.

- By proceeding slowly and constantly cooling the vessel under cold water or in an ice-water bath, add 25 g of concentrated sulfuric acid to 50 g of absolute ethyl alcohol. Place this mixture in a 500 mL flask, then add 50 g of butyric acid and stir gently. Numerous small bubbles appear or, sometimes, the mixture suddenly begins to boil. Two layers of different refractive indices separate. Ethyl butyrate (ethyl butanoate), which smells of pineapple and is therefore used in the food industry and in certain cosmetic products, has been formed. The addition of sulfuric acid is not necessary to obtain this product; a mixture of butyric acid and alcohol alone is sufficient. In that case, however, the alcohol/butyric acid mixture must be heated.

- Mix 1 part methyl alcohol with 1 part H_2SO_4 by slowly pouring the acid into the alcohol while cooling vigorously. Place this mixture in a flask and then add 3 parts butyric acid. Stir rapidly and wait. Sometimes bubbling is observed, while in other cases the liquid slowly becomes cloudy. Two layers appear. The upper layer consists of methyl butyrate (methyl butanoate), which has an apple-like odor and is used as a flavoring agent in both the food and cosmetic industries.

- By grinding in a porcelain or steel mortar, prepare an intimate mixture of 30 g of MnO_2 and 9 g of starch. A second mixture consisting of 30 g of H_2SO_4 and 15 g of ethyl alcohol is prepared by slowly pouring the acid into the alcohol while cooling continuously (under running water or in an ice-water bath). Finally, combine everything in a flask or, better still, in a separatory funnel without fitting the stopper. Ethyl formate, which has a rum-like odor, is formed in the cold. It is used in the food industry as a flavoring agent, but also as a solvent for cellulose acetate (old photographic negatives, motion-picture film, and certain containers).

- Place 1 or 2 cm of CS_2 in a 100 mL beaker. Pour into it, in a single motion, an equal quantity of a concentrated KOH solution in propyl alcohol. The entire mass turns into a plastic yellow-pink material that can afterwards be washed easily with water.

- Allow 3 mothballs of naphthalene to digest for 24 hours in 150 mL of concentrated H_2SO_4. The liquid gradually turns blue and then brown. Pour this liquid into an Erlenmeyer flask (which can later be cleaned more easily than a round-bottom flask). Finally, add potassium dichromate in small spoonfuls, shaking after each addition. Each addition of dichromate causes a rise in temperature, a little foam, and a slight white smoke. As soon as it becomes apparent that the reaction is increasing markedly, that signs of boiling are appearing, and that the smoke is becoming denser, immediately place the Erlenmeyer flask on a concrete slab and move away. Soon a geyser of white smoke erupts while a blackish foam fills the flask. The vessel should afterwards be cleaned roughly with water and then thoroughly with aqua regia.

- In a long test tube (approximately 30 cm), place 2 cm^3 of formalin and carefully pour 1.5 cm^3 of concentrated but non-fuming HNO_3 over it. The liquid fairly rapidly becomes yellow and then the reaction runs away: apparent boiling occurs, droplets are projected, and water vapor, CO_2, and NO_2 are evolved. In fact, formic acid is

formed and subsequently decomposes. By varying the concentration of the HNO_3 and the relative quantities of the reactants, the violence of the reaction can obviously be varied. If fuming nitric acid is used, as described above, the reaction must instead be carried out in a porcelain dish using only a few drops of each reagent.

- Dissolve caustic potash in ethyl alcohol. Then mix this solution with an excess of chloroform. The solution gradually warms and eventually begins to boil while white potassium formate precipitates and potassium chloride remains dissolved in the liquid.

- Place a little 33% H_2O_2 in a porcelain dish. Then add powdered arsenic. Depending on the quantities involved, either progressive boiling or ignition occurs. A very large evolution of heat is observed. If H_2O_2 is present in excess, all of the arsenic is converted into the acidic state and dissolves.

- Pour powdered sugar into a beaker and then add concentrated H_2SO_4. Stir very rapidly with a glass rod until a paste is formed and then leave it on a heat-resistant surface. After one or two seconds, the mass suddenly begins to swell while carbonizing and may even overflow from the beaker. To clean the latter, remove most of the residue with a knife, rinse, wipe with paper towels, and finish with ethyl acetate.
This reaction, which delights YouTube audiences, can also be carried out in the liquid phase and may then be considered even more spectacular. In one beaker prepare 50 mL of a saturated sugar solution and in another 50 mL of concentrated H_2SO_4. Simultaneously pour the contents of both beakers into a tall, narrow 500 mL beaker. The carbonization produces a large quantity of black foam which will overflow extensively. For this reason, the beaker should be placed on a surface that can easily be washed afterwards, or inside a large glass or PVC tray.

DISTRUST AND CAUTION

Certain spectacular chemical reactions require a latency period during which nothing appears to happen. These are perhaps the most dangerous reactions because the operator, believing that the experiment has failed, may be tempted after some time to pick up the reaction vessel or even bring it close to the eyes. Such reflexes must be avoided. In such situations, if one truly believes that the maximum waiting time has been exceeded and that nothing will occur, it is preferable to tip over the vessel using a long pole while remaining at a distance and then to flood the substances with a large bucket of water, provided that water itself does not react with the chemicals involved. If it does, dry sand should be used instead. A large container of sand should always be kept within reach, as sand may also prove very useful for extinguishing the beginning of a

- In a 250 mL beaker, place powdered glucose and then add phosphorus pentoxide (phosphoric anhydride), which has a great affinity for water. Mix the two powders thoroughly with a glass rod and then add two or three drops of water. The material immediately swells, becomes carbonized, and produces smoke and carbon dust. It always emerges from the beaker in the form of a large, very light carbon snake. To restore the vessel to its original condition, remove most of the residue with paper towels, then clean away the greasy material with ethyl acetate and, if necessary, finish with hydrochloric acid.

- In a stemmed laboratory glass, place a layer of potassium chlorate covered by 5 to 6 cm of water together with a piece of phosphorus about the size of half a small pea. Through a long glass tube (at least one meter in length) inclined at 45° and fitted with a funnel at its upper end, allow a few drops of H_2SO_4 to flow very slowly, then a few more, and so on. Each time the H_2SO_4 reaches the chlorate, chlorine dioxide is formed and ignites the phosphorus under water. Although the experiment is largely controlled by the water layer covering the reactants, it remains dangerous and must be carried out slowly and cautiously. This explains the importance of the long tube delivering the acid, which keeps the experimenter at a safe distance.

- Place half a teaspoonful of potassium chlorate in a small porcelain dish and cover it with ethyl alcohol. Using a pipette, add a few drops of concentrated sulfuric acid to the liquid. A vigorous reaction occurs, the alcohol becomes yellowish-green, and chlorine dioxide is evolved. The same phenomenon occurs with each further addition of acid.
WARNING: Do not add too much acid at once, as ignition and dangerous projections may occur.

- On a brick, place a small heap consisting of an intimate mixture of equal parts of flowers of sulfur and copper powder. Ignite it with a torch. The flame rapidly propagates throughout the mass, which becomes compact and black. Copper sulfide has been obtained.
Aluminum sulfide may be prepared in the same way, although the reaction is less obvious.

- Grind charcoal in a mortar until a fine powder is obtained, then mix it with potassium permanganate that has likewise been separately reduced to a fine powder. Mix the two gently in the bottom of a small dish, then wrap the powder, without compressing it, in filter paper so as to form a narrow tube whose ends are twisted closed. Place it on a brick and ignite one end. When the flame reaches the mixture, vigorous combustion occurs, sometimes accompanied by small sparks.

- Fill a beaker to about one-third of its volume with a solution of stannous chloride in HCl and place it inside a second, much larger beaker. The whole assembly should stand on a running magnetic stirrer. Using a burette fitted with a stopcock, allow concentrated HNO_3 to fall slowly and dropwise into the stannous chloride solution. As the drops fall, a faint sound may be heard. Red nitrous fumes are then evolved.

Finally, the reaction accelerates and the liquid may overflow from the beaker. This is why it has been placed inside a larger one, thus preventing the magnetic stirrer from being attacked by the complex tin salts formed during the reaction.

- Take a small 100 mL flask fitted with a standard ground-glass neck and closed with a glass stopper wrapped with a strip of PTFE tape. Pour in approximately 30 g of bromine followed by 10 to 12 g of flowers of sulfur. The sulfur rapidly disappears and the liquid acquires the same repulsive odor as sulfur chloride. Then add 25 to 30 mL of CS_2 and divide the liquid into two portions. Pour the first into a 100 mL beaker and the second into another similar beaker in which a small piece of phosphorus has previously been placed. Shake the second beaker to dissolve the phosphorus in the CS_2. Finally, using a pipette and proceeding cautiously, add ammonia dropwise to each beaker. A very vigorous reaction follows. The liquid boils and copious vapors are evolved. The reaction is even more vigorous in the second beaker, where ignition may occur.

- Place a little chromium trioxide in a porcelain dish. Then add a few drops of concentrated ammonia. The liquid turns yellow and then slowly solidifies into a yellow-red mass.
If, instead of ammonia, a little ethyl alcohol is added, the reaction is violent and green chromium oxide is formed.
If ethyl acetate is used instead of alcohol, the reaction takes some time to begin, but the result is the same.
A similar result may also be obtained by sprinkling sulfur onto the chromium trioxide and heating directly, although this is less spectacular than the reaction with alcohol.

12.8 Sources of Fire or Harmless Explosions

Every year, teenagers (and sometimes even children) attempt to make firecrackers or rocket propellants using common substances that they mix together according to very approximate recipes passed on by word of mouth or found on Internet websites. For many of them, the result is tragedy: they lose their sight, fingers, an arm, or even their lives. This is the dramatic side of chemistry that causes many people to distrust its practice.

One should never forget that few things are more exciting to a human being than trying to discover something that he believes is being deliberately hidden from him. This is part of the natural learning process and is in no way a form of unhealthy curiosity. Therefore, rather than attempting to conceal certain subjects from children or teenagers who may not yet be ready to discover and understand them by themselves, it is far better to explain such matters clearly and frankly as early as possible. Doing so may prevent serious misunderstandings that could result either in completely erroneous conclusions or in various psychological or physical dangers.

This is particularly true in the field of sex education, but it is equally true in chemistry.

For this reason, young people should always be informed of the dangers associated with certain chemical experiments, especially those involving oxidizing or explosive mixtures. Since parents do not always possess the scientific knowledge required for this essential educational task, it is important that such instruction be provided by teachers within the schools themselves. It is essential to demonstrate to young people that even very small quantities of substances can produce loud explosions or significant projections, and that extreme caution must therefore always be exercised when handling or mixing them. This is all the more important because some mixtures are particularly sensitive to friction, impact, heat, or ignition.

The examples that follow are intended to illustrate, under carefully controlled conditions, the potentially hazardous nature of energetic chemical mixtures. When carried out exactly as described and with appropriate precautions, such demonstrations may be spectacular while remaining far less dangerous than many procedures now freely available on the Internet or discussed imprecisely by well-meaning but poorly informed amateurs. I shall begin, quite logically, with examples involving ordinary weed killer (sodium chlorate) or potassium chlorate throat lozenges. In all cases, safety goggles should be worn, together with clothing that covers as much of the body as possible.

A NOTE TO ASPIRING PYROTECHNICIANS

Readers interested in explosions will quickly realize, from what follows, that I have deliberately limited myself to demonstrations that are certainly spectacular but of little practical value for the manufacture of large firecrackers or, worse still, improvised explosive devices. Anyone attempting to construct such devices on the basis of the descriptions contained here would generally become their first—and possibly last—victim.

Many chemistry books contain descriptions or information that appear to make the preparation of stable, transportable explosives seem relatively straightforward. Nitrocellulose, for example, is often presented in this way. However, readers should remember what was explained at the beginning of this book: many experimental descriptions are incomplete, imprecise, or sometimes even incorrect. This observation also applies to the preparation of supposedly stable explosive materials. Consequently, anyone who values his own life should not expect to find reliable methods for manufacturing large firecrackers or improvised bombs either in the pages that follow or in conventional chemistry textbooks.

- The following experiment helps explain how early matches were made: prepare a very stiff paste from a mixture of starch and potassium chlorate, using very little water. Dip wooden splints into the paste and allow them to dry. If the coated end is dipped into H_2SO_4, it ignites.

- Place an intimate powdered mixture of potassium chlorate and one of the following—sulfur, sugar, starch, or sawdust (choose only one of these four, not all of them together!)—into a small glass dish. Prepare the mixture by stirring it very gently and briefly while holding the dish with long tongs. The volume of the mixture should not exceed a small pile measuring 2 cm in diameter and 5 mm in height. Then, let a few drops of concentrated H_2SO_4 fall onto the mixture. The whole thing ignites vigorously. The ignition itself is not dangerous; the danger lies in the preparation process, as this mixture—like others of its kind—can explode due to compression or simple friction between its components while being stirred! Hence the use of tongs to keep your hand away from the dish.

- Place a small, thoroughly mixed (but not packed) mound of sodium chlorate (a total weedkiller) and sugar—flour or sawdust can be used instead of sugar—on a brick or flat stone. The mixture should be no larger than a large pea. Strike it with a hammer; the mixture will explode like a small firecracker. As with other similar activities, it is wise to wear ear protection.

- Place an intimate mixture of powdered sugar and potassium chlorate on a refractory stone with a hollowed-out center. Arrange the mixture in a line rather than a heap, without packing it down (a line measuring 5 cm by 0.5 cm is sufficient). Prepare the mixture in a small dish by stirring it very briefly while holding the dish with long tongs. Be sure to avoid compressing the particles during this process, as the mixture is sensitive to impact and to heat generated by the friction of particles rubbing against one another. Also, be aware that this mixture can react spontaneously with certain metals; therefore, use only glass, porcelain, or refractory ceramic containers. Finally, touch the mixture with a long metal rod heated to red heat. Rapid ignition occurs, producing a brilliant white flame and a large amount of smoke.

- Prepare an intimate mixture of zinc powder and half its weight of flowers of sulfur. Place this mixture in a porcelain boat or on a brick. Touch it with a copper wire heated to red heat in the flame of a blowtorch held at a distance. Ignition is violent. If a small amount of the original mixture is introduced into the flame on a copper rod, a very brief green flare-up occurs. This same mixture detonates if placed on a stone in a pea-sized heap and struck with a hammer.

- Prepare a fairly stiff paste made of zinc powder, kieselguhr, and carbon tetrachloride. Spread it out in a small porcelain tray and ignite one end using a blowtorch. The paste then burns from end to end, releasing dense white fumes and leaving an ashy residue.

- In a small dish, mix equal parts of flowers of sulfur, powdered carbon, and potassium iodate. Pile the mixture onto a brick and touch it with a steel wire heated to red-hot in a blowtorch flame. The mixture ignites, producing mauve iodine vapors that should not be inhaled (Figure 151).

Figure 151

- A mixture of magnesium and iodine ignites upon contact with water, which can be poured onto it from a safe distance using a long pipette or a wash bottle.

- A mixture of zinc powder and iodine ignites and releases iodine vapors when a few drops of water are squirted onto it from a distance using a wash bottle.

- Place an intimate mixture of 4 g of ammonium nitrate and 1 g of ammonium chloride—the components of which have been finely pulverized separately in a mortar—into a small dish. Sprinkle zinc powder over the mixture. Add a few drops of water. Ignition, intense heat, and smoke ensue.

- Place a small amount of potassium nitrate, sulfur, and antimony sulfide (Sb_2S_3) into a porcelain dish. All three substances must be in the form of a fine powder. Mix them by gently shaking the dish with long tongs, taking care to avoid any jarring movements. Then, after gathering the mixture by tilting the dish, ignite it using a red-hot copper rod. The combustion is vigorous, producing a brilliant white flame. Once the reaction is complete, red traces remain in the dish (Figure 152).

Figure 152

- Separately crush NaCl and then potassium permanganate using a porcelain pestle, and place a small amount of each at the bottom of a crucible, stirring gently to obtain a thorough mixture. Add a few drops of H_2SO_4 to the mixture using a pipette and immediately step back. A brown gas will be released, and the reaction will accelerate rapidly, producing an abundant black cloud of very fine MnO_2.

- Place a pea-sized amount of potassium permanganate in a 25 or 50 mL beaker. Add three drops of concentrated sulfuric acid. Finally, carefully add a single drop of ethyl alcohol. Ignition occurs.

- A drop of an SO_2 solution in ethanol is placed on a small pile (pea-sized) of peat. An explosion occurs.

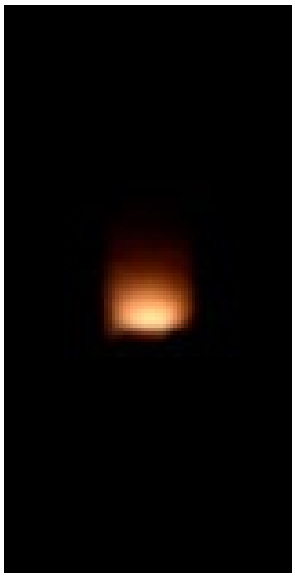


Figure 153

- Take a test tube approximately 30 cm long with a diameter of 15 to 18 mm and secure it vertically using a stand and clamp. First, pour in concentrated sulfuric acid to a depth of two centimeters. Next, using a pipette with its tip touching the inner wall of the test tube, carefully pour 94% ethyl alcohol onto the acid. As the alcohol flows slowly down the inner wall onto the acid, it will not mix with it. Continue pouring until the alcohol layer is four centimeters deep. Finally, after positioning a protective screen, drop a crystal of potassium permanganate—roughly the size of a split pea—into the test tube. A reaction immediately occurs at the interface between the two liquids. Dimanganese heptoxide forms, producing sparks as it oxidizes the ethanol into CO_2. Ozone is also produced. Once the reaction has begun, the room is darkened, and one waits. Gradually, sharp sounds are heard, sometimes accompanied by sparks of varying intensity (Figure 153). This reaction can last more than twenty minutes. After this time, the test tube can be carried—without shaking—to a location where it can be tilted and gradually emptied onto absorbent soil. Caution is required when tilting the tube, as the reaction may flare up quite vigorously. The residue must then be thoroughly flushed with water.
WARNING : Never pour potassium permanganate directly in H_2SO_4 because this mixture is very unstable and explosive.

- The dangers associated with preparing and using spontaneously flammable phosphine (hydrogen phosphide) were described on page 108.
However, there is a radically different way to safely prepare this substance and observe its primary characteristic—a method that, to my knowledge, is not mentioned in any chemistry textbook. It essentially involves reversing the experimental setup by conducting the procedure in the open air rather than within the oxygen-free atmosphere of a flask.
To do this, one takes a dish containing a layer of concentrated NaOH solution—at least a centimeter deep—and places a few small pieces of yellow phosphorus in it. The dish is set outdoors in the open air, and an infrared radiator is positioned above it. This device gradually emits increasingly intense infrared radiation until sparks and then flashes of light erupt on the surface of the alkaline solution, releasing a fairly dense, toxic white smoke; due to the heat, this smoke rises rapidly, posing little risk of inhalation (Figure 154).

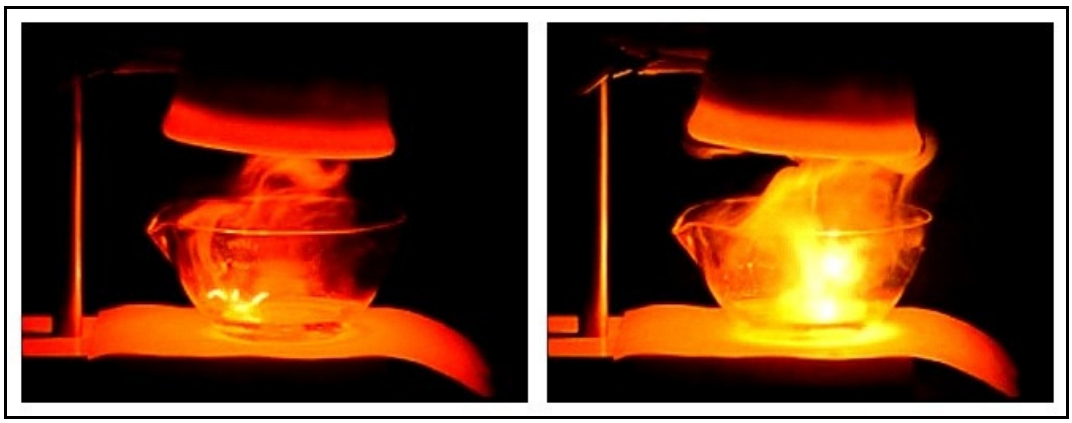


Figure 154

- Place a few small zinc scraps and some small pieces of yellow phosphorus—with a total volume no greater than half a pea—into a small glass dish (approx. 4 cm in diameter). Pour in enough diluted H_2SO_4 to submerge the contents. Ideally, the acid should be pre-heated to around 40°C. Hydrogen phosphide is immediately released in swirls of white smoke. In some cases, spontaneous ignition occurs, accompanied by a yellow flame and minor spurting (Figure 155). In all instances, the garlic-like odor of phosphine is clearly perceptible. However, avoid inhaling the gas, as it is a dangerous poison.

Figure 155

- Place a piece of phosphorus on iodine flakes. Ignition occurs rapidly.
Various sources state that phosphorus and iodine—placed in separate dishes under a glass bell jar—will ignite. In reality, this rarely happens! It requires optimal conditions regarding temperature, quantities of substances, and the volume of the bell jar—not to mention plenty of time! Nevertheless, these two substances should never be stored in close proximity to one another.

- Pour 5 cm of concentrated HNO_3 into a test tube (approximately 20 cm long and 25 mm in diameter), followed by 1 cm of water, taking care to minimize mixing

between the two. Next, drop in a few small fragments of phosphorus—ensuring the total volume does not exceed the size of a pea. Finally, drop half a cubic centimeter of powdered potassium chlorate into the test tube, which is held vertically by a clamp and stand. As the powder sinks into the liquid, small deflagrations are heard, and flames are occasionally visible at the bottom of the liquid.

- Potassium nitrate and a piece of phosphorus are placed in a porcelain boat; the phosphorus is then ignited using a long, heated copper or iron wire. It is observed that the flame intensifies when the phosphorus comes into contact with the nitrate.

- In a small, tightly sealed vial, dissolve a piece of phosphorus the size of half a pea in 50 mL of CS_2. Then, using a PVC pipette, take a few drops of this solution and pour them onto a piece of filter paper. Simply waving the filter paper in the air causes the solvent to evaporate, and the paper immediately bursts into flames. This experiment—which is very spectacular yet poses little danger—can serve as the basis for a magic trick where paper is made to catch fire after appearing to be "wet." It also highlights the danger of allowing a phosphorus-in-CS_2 solution to evaporate by failing to quickly reseal the vial containing it...

- Prepare a solution of phosphorus in CS_2 and pour a few drops onto a pea-sized pile of potassium chlorate placed in a PVC dish. Once the CS_2 has completely evaporated an huge explosion occurs.
WARNING: The vessel used must not be made of brittle material such as porcelain, as sharp fragments could be scattered in all directions and cause injury. The reaction is particularly dangerous because it does not always occur precisely at the moment the carbon disulfide appears to have evaporated. The chlorate gradually turns yellow, and the reaction takes place unexpectedly after some time. It is therefore essential to keep a safe distance.

- Pour a small amount of turpentine into a porcelain dish placed in the open air in an unobstructed area. Then, add a few drops of ordinary HNO_3. The liquid turns yellow. Stay well away from it. After a few minutes—sometimes ten or more—the expected reaction occurs suddenly, accompanied by a sound like a firework rocket. The orange substance remaining in the dish can be easily cleaned off with alcohol. This reaction is dangerous because it is unpredictable. With fuming HNO_3, the reaction is instantaneous (see page 342).

- Here is another, more spectacular way to conduct a similar experiment. Pour 10 mL of turpentine into a 300–500 ml beaker. In a separate 50 mL beaker, pour a mixture of 15 mL of concentrated (but not fuming) nitric acid and 5 mL of concentrated sulfuric acid. Quickly pour this mixture into the large beaker and immediately step back. A hissing sound is heard, followed by the appearance of black smoke and, finally, tall flames. Varying the proportions of the acids (for example, by using a fifty-fifty mix) and the amount of turpentine can yield different results: the reaction might occur after a few seconds or, alternatively, suddenly after a full minute. The noise may resemble that of a flamethrower, and copious, glowing,

toxic vapors are released. This is therefore the type of experiment that should be performed using only small amounts of reactants and while keeping a safe distance from the flasks being used. Ultimately, the reaction flask contains a hard, porous red substance that can be gently removed from the glass using the scouring pad side of a sponge (Figure 156).

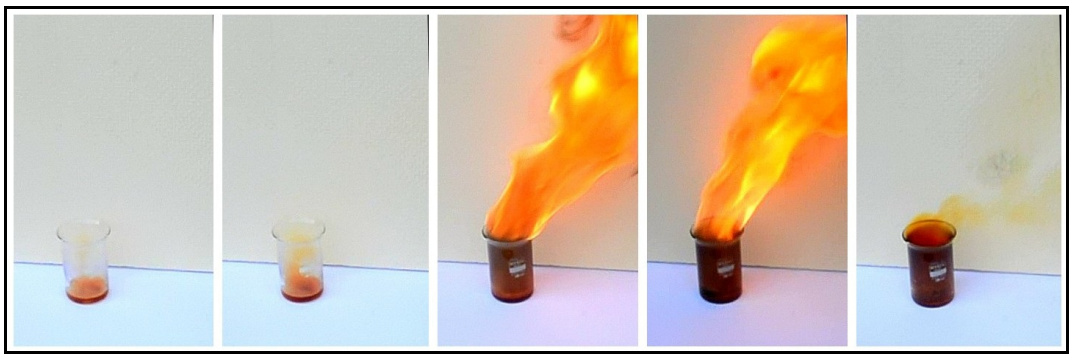


Figure 156

- Here is how to successfully perform the famous "Pharaoh's serpent" experiment, often described in literature or online...
Pour 15 mL of concentrated HNO_3 and 3 mL of mercury into a 150 mL Erlenmeyer flask. Since copious nitrous fumes are immediately released, place the mixture outdoors or connect it to an exhaust tube leading outside. Wait for the reaction to finish. Typically, a moist white crystalline mass remains in the flask, accompanied by some reddish-brown fumes. Then, add water, taking care not to add too much so that no precipitate forms. Mercury nitrate remains dissolved in water as long as the solution stays acidic. Pour the resulting liquid into a second Erlenmeyer flask or a wide graduated cylinder. Add a solution of potassium or ammonium thiocyanate. A fairly heavy white precipitate forms immediately. Stir the mixture and pour it into a crystallizing dish or porcelain evaporating dish. Let it settle, then pour off the excess liquid. Then, work the white paste by adding a small amount of solid potassium nitrate and solid gum arabic. Finally, using filter paper or paper towels, try to absorb as much liquid as possible and place the paste on a radiator. As it dries, compact the white solid using a PVC spatula. Once the solid is thoroughly dry, ignite it outdoors using an ordinary match. This produces the famous "Pharaoh's serpent" effect, where the mass elongates into various tube- and ribbon-like shapes (Figure 157). Ignition must

Figure 157

be performed outdoors to avoid inhaling the fumes produced. The inside of the dish used for ignition becomes coated with black soot.
Another, simpler method involves reacting potassium or ammonium thiocyanate directly with a mercury salt to obtain the appropriate precipitate, which is then decanted and dried.
A ready-made kit that simply requires ignition can be purchased at certain joke shops.

- Small carbon "snakes" emerging from the flames can also be produced easily as follows: mix powdered sugar and sodium bicarbonate together. Then, pack this mixture to the brim of a small container—such as a test tube—measuring 3 or 4 cm in height and 15 mm in diameter. Douse it with methyl or ethyl alcohol until the mixture is thoroughly saturated. Finally, set it alight.

- And, to conclude this chapter, water that creates a flame. In a porcelain dish, place a mixture of approximately 10 g of powdered zinc, 4 g of ammonium nitrate, and 1 g of magnesium chloride. Mix thoroughly, then add a few drops of water. A hissing sound is heard, after which the mixture ignites. When the reaction is complete, a strange-looking solid remains (Figure 158).

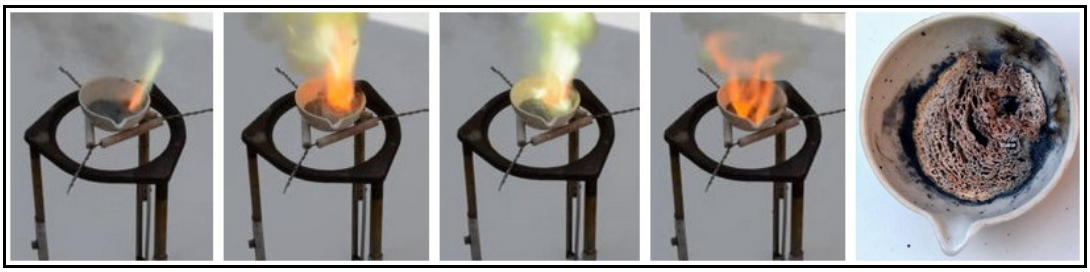


Figure 158

Chapitre 13 - Photochemical Reactions

- Here is a remarkable experiment in which light plays an essential role. Under subdued lighting, prepare a solution of ascorbic acid (vitamin C). Add a small quantity of powdered methylene blue and shake until a vivid blue coloration is obtained. Place the flask in direct sunlight or illuminate it with a powerful lamp. The blue color disappears almost immediately. If some particles of methylene blue have not yet completely dissolved and the solution is shaken further, a blue trail can be seen behind them, but it vanishes very quickly.When the flask is placed back in the dark, the blue coloration gradually returns, although less vividly than before. Further exposure to light causes it to disappear again. The experiment may thus be repeated several times, but the successive color changes tend to become less pronounced.

- Prepare three test tubes, each containing about 3 mL of water. In the first, dissolve a spatula-tip quantity of ferric chloride. In the second, dissolve a spatula-tip quantity of potassium ferricyanide. In the third, dissolve a spatula-tip quantity of oxalic acid. Pour the contents of the first two test tubes into a small beaker to obtain a clear brown solution. Then, protected from direct light, add the contents of the third test tube. An emerald-green solution is produced. Pour this solution onto a piece of filter paper. When exposed to light, the paper rapidly turns blue. The experiment becomes even more striking if part of the filter paper has previously been covered with a piece of cardboard. In that case, only the illuminated area undergoes the color change.

- Mix a solution of potassium iodide with a solution of lead acetate. A lumpy canary-yellow precipitate is formed. Add a little starch paste and place the mixture in direct sunlight against a wall. The side exposed to the sun gradually develops a mauve coloration.
Similar effects may be obtained with a simple mixture of silver nitrate and salt water. In this case, the initially white precipitate gradually turns bluish and eventually becomes mauve or black, depending on the duration of exposure.
Here again the experiments become more striking if part of the precipitates have

previously been covered with a piece of cardboard in order to obtain only a partial coloration.

- Under subdued lighting, dissolve a small quantity of iodoform in a few millilitres of ethyl alcohol contained in a tightly stoppered colorless glass test tube. Place the tube in direct sunlight. The solution slowly changes from dark yellow to orange, then red, and finally violet. An inactinite test tube may be used for comparison.
The same experiment may also be performed by dissolving the iodoform in carbon disulfide or ether. Because the solubility is greater in these solvents, the color change occurs even more rapidly. It is caused by the liberation of iodine.
Of all iodine compounds, iodoform is probably one of the most light-sensitive, even in the solid state. It should therefore be stored in a brown bottle and kept in a dark place.

Simple Photographic Images:

Working under inactinic light or very subdued illumination, any of the precipitates described above may be heated in an aqueous solution of gelatin or, preferably, agar-agar. The resulting mixture is then poured into a Petri dish and allowed to cool in complete darkness.

A cardboard mask should be prepared beforehand so that it fits exactly inside the Petri dish and contains a number of cut-out shapes. After twenty-four hours, place this mask on the solidified gel and immediately expose the dish for a few minutes to sunlight or to the light of an ordinary incandescent lamp.
Under subdued lighting, it will then be possible to observe that only the exposed areas have changed color. A crude form of "photograph" has thus been produced. Unfortunately, the image cannot be preserved indefinitely, since continued exposure to light will gradually affect the entire surface of the Petri dish.

Chapter 14 - Reactions on Heating in the Presence of at Least One Liquid

14.1 Reactions with Metals or Metalloids

Iron, Zinc, Copper, Tin, Lead

– Boil iron powder for a long time in a sodium cyanide solution, then establish, by comparing the various precipitates obtained, that sodium ferrocyanide has formed.

– Heat glacial acetic acid with iron granules. The liquid turns red fairly quickly. Allow it to stand and cool, then dilute it with water to obtain an orange liquid. Add aqueous ammonia. The mixture becomes warm and ammonium acetate is released in the form of white fumes, since not all the acid has yet been neutralized. The liquid then becomes cloudy, and a red precipitate of iron(III) hydroxide forms.

– A strip of zinc immersed in an aqueous NaOH solution reacts very little, if at all. However, when the solution is heated, a vigorous evolution of hydrogen soon occurs. Sodium zincate is formed. With KOH, the reaction is less obvious.

– Place a walnut-sized piece of alum in a 500 mL flask and add 200 to 250 mL of water, together with a zinc strip measuring 1 to 2 cm^2. Heat. As the solution approaches its boiling point and the alum dissolves, small bubbles can be seen forming on the zinc. Eventually, a torrent of extremely fine bubbles is released from the zinc strip, forming what looks like a cloud above it. This cloud consists of hydrogen.

– In a borosilicate glass flask, boil water containing iodine and an excess of zinc powder. The iodine gradually disappears as zinc iodide forms.

– Immerse a copper strip in a flask containing a mixture of sulfurous acid solution and HCl. Heat. The copper becomes coated with a black layer of copper sulfide.

– Pour a very dilute hydrochloric acid solution into a test tube and place a small, brightly polished copper strip in it. Then add a small spatula tip of arsenic trioxide and heat to boiling. The copper strip becomes coated with a bright metallic layer resembling silver or nickel.

– Place a piece of copper foil approximately 1 cm^2 in size in a test tube. Pour concentrated sulfuric acid over it, then add a small amount of sodium nitrite. Nothing happens. Heat very slowly. A very dark violet-purple color gradually detaches itself from the copper and eventually spreads throughout the liquid. Continue heating. White fumes escape from the test tube, and the purple color disappears, giving way to a grayish-yellow liquid. Stop heating. A gray oxide rapidly settles to the bottom beneath a green liquid. Allow to cool, then pour off most of the green liquid. Add water. A beautiful blue solution appears, containing suspended grains of black oxide.

– When heated, tin reacts vigorously with concentrated hydrochloric acid.

– Lead reacts with sulfuric acid when heated, but not in the cold. This is why lead-lined vessels were once used for the manufacture of sulfuric acid.

– A piece of lead heated in formic acid reacts with it. The liquid becomes cloudy.

Magnesium and Aluminum

– In a boro 3.3 test tube, mix magnesium turnings with mercury. Nothing happens except that the turnings become black. Then heat the mercury. A kind of boiling occurs, and the metal becomes dull gray and less mobile. It now adheres to the walls of the test tube. It can be cleaned with nitric acid.
WARNING: the reaction is then violent and produces abundant toxic reddish-brown fumes. Some of the mercury can thus be recovered.

– Place small magnesium turnings in a little water and heat to boiling, then remove the flame. When boiling ceases, the magnesium can be seen continuing to react with the water, producing hydrogen. This is why water must never be used to extinguish a fire occurring near stored magnesium.

– Place aluminum in concentrated nitric acid. Nothing happens. Heat. Nitric oxide is evolved and is converted into nitrogen dioxide on contact with the air. Aluminum nitrate is formed.

– In a small flask connected to a bottle containing limewater, heat a solution of sodium carbonate with a small amount of aluminum powder. The mixture begins to foam, and carbon dioxide is evolved while alumina is formed. The same experiment carried out with sodium sulfide produces hydrogen sulfide instead. It should be noted that, in this latter case, the gas evolution already begins in the cold and quickly

becomes vigorous.

– Aluminum reacts neither by cold nor by hot acetic acid. However, if sodium chloride is added to slightly diluted acetic acid, the aluminum tarnishes all the more rapidly when the reaction is carried out at a temperature close to boiling. This once again illustrates the danger of certain types of cooking in aluminum cookware.

– Aluminum powder placed in aqueous hydroiodic acid does not react. If heated, however, the reaction becomes clearly apparent.

– Some chemistry books state that an alkaline cyanide solution rapidly attacks aluminum at room temperature. I nevertheless had to heat the mixture before I could observe this reaction.

– Place a fairly concentrated sodium carbonate solution in a large test tube, then drop in a small ball of aluminum foil. Nothing happens. Heat. The liquid soon begins to foam vigorously. If the test tube is removed from the flame, gas evolution can be seen continuing around the aluminum ball while it gradually turns black. When the reaction is complete, the previously clear solution rapidly becomes milky and then deposits a white, flocculent precipitate. This is in fact a complex reaction. It is thought that the aluminum is first attacked by water, forming hydrogen and aluminum hydroxide, which then reacts with the carbonate to form an aluminate. The mechanism, however, is still debated (see Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London, Longmans, 1929, Vol. V, p. 208).

Chromium

– Concentrated sulfuric acid does not react with chromium at room temperature. When heated, the reaction is brief and then stops, while the liquid acquires a slightly dirty yellow color. Dilute sulfuric acid, however, already reacts in the cold. Heating accelerates the reaction still further. The solution first becomes sky blue, then deep blue-green. After cooling, its color slowly changes to violet-purple.

– When heated with concentrated hydrochloric acid, a small amount of chromium powder gives a beautiful green solution of chromium(II) chloride. If this solution is added dropwise to a sodium hydroxide solution or to a potassium ferricyanide solution, nothing remarkable is observed. In contrast, when added to a potassium ferrocyanide solution, it immediately produces a yellowish-green precipitate, while addition to a sodium thiocyanate solution gives a bluish coloration accompanied by abundant white fumes. This color then gradually changes to mauve-lilac.

Mercury

– Place 45 g of mercury, 15 g of sulfur, 60 mL of water, and 9 g of KOH in a beaker.

Heat the mixture in an 80 °C water bath while stirring continuously until the mercury has almost completely disappeared. Allow the mixture to settle. Pour off the reddish liquid (mercury polysulfide) and keep the black powder that has settled. This powder is mercury sulfide (cinnabar). Heat it in a small Kjeldahl flask whose neck is naturally cooled by the surrounding air. Droplets of mercury appear on the cool walls of the neck.

– Prepare a mixture of 30 g of mercury and 10 g of flowers of sulfur by grinding them together in a mortar until a black powder is obtained. Pour this powder into a large test tube, then add a cooled solution prepared by dissolving 6 g of potassium hydroxide in 40 mL of water. Mix thoroughly with a glass rod and place the test tube in an 80 °C water bath. The liquid gradually turns red while red solid deposits form on the glass. This is artificial mercury sulfide, the pigment once known to painters as vermilion.

– Pour two drops of mercury into a test tube and cover them with a few centimeters of an aqueous solution of chromic oxide (chromium(VI) oxide). Heat. The solution soon becomes cloudy, and green chromium(III) oxide precipitates.

– Heat an aqueous solution of sodium thiosulfate with two drops of mercury. The mercury eventually acquires a bronze color. Pour off the solution, rinse with distilled water, then add two or three drops of hydrochloric acid. The smell of rotten eggs indicates that mercury sulfide had been formed.

– Some authors state that mercury and aluminum do not amalgamate, while others claim that they amalgamate readily. As is often the case, the truth lies somewhere between these two extreme opinions. To amalgamate mercury and aluminum, proceed as follows: place a small amount of mercury and aluminum powder in a test tube, fill it with carbon dioxide, and close it with a stopper fitted with a valve to relieve any excess pressure. A rubber or silicone cap-type stopper is suitable if pierced beforehand with a pinhole. Heat the mercury and aluminum powder to boiling and maintain this temperature for one or two minutes. Then allow the mixture to cool and, if desired, let it stand for 24 to 48 hours. Afterwards, pour a little water into the test tube. A slow reaction begins, accompanied by the evolution of gas, demonstrating that an amalgam had indeed been formed.

Cobalt and Titanium

– Heat a small amount of cobalt powder with bromine water. The solution turns violet.

– Heat a small piece of cobalt in formic acid in a test tube. The solution becomes slightly pink owing to the formation of cobalt formate. Add a potassium ferrocyanide solution to this liquid. A beautiful, transparent electric-blue solution is obtained.

– Pour hydrochloric acid into a small flask containing titanium. Heat gently until hydrogen begins to evolve. Cover the flask with a piece of Parafilm pierced with a fine needle hole to allow the hydrogen to escape while preventing air from entering. Thereafter, heat the mixture several times until as much of the titanium as possible has dissolved and the increasingly mauve, or even blue, solution has become progressivelly less acidic. A mauve solution of titanium(III) chloride has thus been obtained. Filter and dilute it with a slightly larger volume of water. Pour enough into a test tube to obtain a depth of about 3 cm and add a few drops of hydrogen peroxide. The solution turns deep red. Then add sulfurous acid. The solution becomes colorless while warming up, yielding titanium(IV). If a little of the aqueous $TiCl_3$ solution is added dropwise to baryta water, a white precipitate is obtained. If a test tube is filled with a few centimeters of the $TiCl_3$ solution and aqueous ammonia is carefully poured on top, a black precipitate forms.
More interesting, however, is the following experiment. Pour a small amount of potassium chromate solution into a test tube, then add the $TiCl_3$ solution drop by drop. A precipitate forms and passes through several successive colors. It then dissolves in an excess of $TiCl_3$, while the color of the solution changes from yellow to green and finally to mauve.
WARNING: Even in hydrochloric acid, a $TiCl_3$ solution does not keep indefinitely.

– Heat titanium powder gently with concentrated sulfuric acid. Gas is first evolved while the liquid becomes transparent mauve. The gas evolution then ceases, and the liquid turns opaque cornflower blue. After standing, a cornflower-blue deposit forms beneath a brownish supernatant liquid.
With slightly diluted sulfuric acid, a much larger, rather mauve deposit is obtained. If concentrated hydrochloric acid is added to the still blue deposit containing sulfuric acid, a vigorous evolution of hydrogen chloride first occurs (because of the reaction between the two acids), after which the liquid slowly regains its original mauve color. If concentrated nitric acid is added instead, the liquid clears within barely a minute, leaving only a transparent solution slightly yellowed by nitrogen dioxide. However, if a large amount of the mauve deposit is used, separated as much as possible from the sulfuric acid and therefore almost compact, and only a small amount of concentrated nitric acid is added, the liquid turns green in less than a minute, with only a slight evolution of nitrogen dioxide.
If the titanium is initially treated with more dilute sulfuric acid, the evolution of gas lasts longer and the solution becomes mauve while remaining perfectly clear. When aqueous ammonia is added to this mauve solution, a blue precipitate forms and turns white within a few minutes.
Potassium ferrocyanide and potassium ferricyanide solutions both first produce a yellow color change and then a yellow precipitate. Ammonium sulfide solution, on the other hand, gives a greenish precipitate. Upon addition of an oxalic acid solution, the mauve solution turns dark yellow. A hydrochloric solution of antimony trichloride completely decolorizes the mauve solution, whereas hydrogen peroxide produces a blood-red color. A strip of zinc immersed in the mauve sulfuric solution immediately causes the evolution of hydrogen together with the formation of a brown, then black, precipitate. Iron powder, on the other hand, simply causes

hydrogen to be evolved, while a strip of copper has no effect. If a piece of antimony is placed in the mauve sulfuric solution of titanium sulfate, nothing happens in the cold. Upon heating, the liquid becomes milky and then deposits a white precipitate. NOTE: The mauve sulfuric solution does not keep. Over the course of several weeks, it gradually loses its color while a white deposit adheres to the walls of the bottle.

Molybdenum

– When heated with concentrated sulfuric acid, a small amount of molybdenum powder gives a beautiful blue solution that, if heating is continued while stirring to prevent excessive formation of sulfur trioxide, turns a beautiful emerald green. Upon cooling, the solution becomes blue again. When reheated, it turns green once more. If the cooled blue solution is poured into distilled water, it first becomes green and then a beautiful golden yellow that gradually fades. Added dropwise to a potassium ferrocyanide solution, it rapidly produces a rather dark brown coloration, whereas in a potassium thiocyanate solution it gives an orange color that gradually turns red. The addition of a few drops of antimony trichloride in hydrochloric acid to these two colored solutions produces beautiful pistachio-green and raspberry-red colors, respectively. These colors are only temporary, however, because the corresponding precipitates (yellow and white, respectively) settle rather quickly.

– Place a small spatula tip of molybdenum powder into an ordinary test tube. Add three drops of water followed by about 2 cm of concentrated nitric acid. A slight reaction occurs, and the liquid turns yellow. Heat. Reddish-brown fumes are evolved, and the solution becomes red. Continue heating. A yellowish-white precipitate of molybdenum trioxide forms. It adheres to the walls or settles to the bottom. Continue heating until you are certain that no acid remains while still leaving a little unreacted molybdenum. Add sodium hydroxide solution followed by 2 mL of hydrogen peroxide. Heat again. The liquid then becomes a beautiful, transparent canary yellow.
If the test tube is not thoroughly cleaned and concentrated hydrochloric acid is added, this precipitate dissolves even in the cold, but much more vigorously when heated, with the evolution of chlorine (true aqua regia is then formed). The resulting golden-yellow solution, after dilution, becomes paler with sodium hydroxide, gives a dirty brown precipitate with sodium sulfide, and a beautiful orange-pink coloration with sodium thiocyanate.

– When heated in dilute nitric acid, molybdenum first gives a yellow solution and then one of brick-red color. A precipitate subsequently forms and settles.

– Molybdenum heated in an aqueous solution of iodic acid (HIO_3) liberates iodine, causing the solution to turn brown. Heated alone, iodic acid does not produce this reaction.

– Place molybdenum together with molybdenum(VI) oxide (MoO_3) in water. Heat

at a gentle boil for quite some time. Allow the mixture to settle for at least 12 hours, or centrifuge it. The characteristic blue molybdenum oxide ("molybdenum blue") has formed.

Vanadium

– Sulfuric acid reacts with vanadium only when it is concentrated and heated. A cloud of sulfur trioxide is soon evolved, while the solution, after briefly becoming yellowish, turns grayish. After settling, a yellow liquid remains above the solid. It consists of an acidified aqueous solution of what is often incorrectly called vanadic acid (V_2O_5).

– Vanadium powder heated in a saturated aqueous solution of potassium chlorate produces a yellow solution because vanadium(V) oxide (V_2O_5) and potassium chloride are formed.

Tungsten

– Even when heated, tungsten shows no visible reaction with either nitric acid or hydrochloric acid. No visible reaction is observed with acetic, oxalic, or tartaric acid either. It does, however, react slightly with sulfuric acid. Place a small amount of tungsten in a small flask or Erlenmeyer flask and cover it generously with concentrated sulfuric acid. Heat gently, then allow the mixture to boil. The liquid gradually acquires a faint blue tint before becoming milky white. Pour out the contents and rinse the flask. A bluish film can be seen adhering to the glass. As for the milky liquid, it settles extremely slowly, leaving a grayish-blue deposit.

– Aqua regia reacts with tungsten when heated. Place approximately one-quarter of a cubic centimeter of tungsten powder in a 100 mL flask and add aqua regia containing an excess of hydrochloric acid. Heat gently to initiate the reaction. The liquid soon turns orange and then yellow. After a considerable time, the reaction ceases. Swirl the flask and pour the contents into a tall test tube. Allow the solid to settle and pour off most of the liquid. Add water and allow the mixture to settle again. Repeat this operation several times until the wash water is no longer acidic. A yellowish precipitate remains, possibly mixed with tungsten that has not reacted. It consists of tungsten trioxide (WO_3), which, in its hydrated form, is known as tungstic acid (H_2WO_4). Next, add aqueous ammonia drop by drop. The pale yellow precipitate disappears because ammonium tungstate is formed. If hydrochloric acid and a small amount of zinc are added to this solution, it turns blue. If hydrochloric acid is added first, followed by a small amount of tin(II) chloride, and the mixture is heated, a grayish-blue precipitate is obtained.
WARNING: The ammonium tungstate thus formed may contain excess ammonia. Hydrochloric acid should therefore be added slowly until no further reaction occurs (white fumes of ammonium chloride).

If the tungsten trioxide obtained initially is heated, it first turns orange and then returns to its original pale yellowish-white color. It gradually dissolves in hydrogen peroxide to give a clear solution.

Bismuth

– Place a piece of bismuth in concentrated sulfuric acid. Nothing happens. Heat. The attack begins. Stop heating. The reaction gradually slows down, and a white deposit forms in the test tube.

Antimony

– Heat concentrated sulfuric acid with pieces of antimony while allowing the sulfur dioxide produced to escape. The liquid first becomes pink to mauve, then perfectly transparent, and finally slightly yellowish. If heating is stopped, the contents of the flask gradually solidify into a white crystalline mass of antimony sulfate. Pour water into the flask. A white precipitate of antimony oxide forms.

– Heat antimony with nitric acid. Nitric oxide is evolved and is converted into nitrogen dioxide on contact with the air, while antimony nitrate is formed. If this product is calcined, antimony(V) oxide (Sb_2O_5) is obtained. It can then be dissolved in hydrochloric acid to form antimony pentachloride ($SbCl_5$).

14.2 Reactions with Nonmetals

Charcoal

– Place nitric acid and a small amount of charcoal in a flask. Even at room temperature, the gradual appearance of red fumes can already be observed. Heat. The flask gradually fills with increasing amounts of red nitrous fumes. Pass the evolved gases through a Drechsel bottle containing a little water to absorb the nitrogen oxides, then through a second bottle containing baryta water, which turns milky in the presence of carbon dioxide.

Sulfur

– Every young chemist knows—or should know—that sulfur may exist in the stable form of a powder, in blocks, or in the colloidal state. It can also exist temporarily as soft, elastic sulfur when molten sulfur is poured into cold water. However, sulfur can also occur in crystalline form.
To obtain it in this form, chemistry textbooks generally recommend heating sulfur

in a crucible and allowing it to cool there. There is, however, another and simpler method. Place approximately 10 g of sulfur and 100 mL of toluene in an Erlenmeyer flask. Place the flask in a water bath on a heated magnetic stirrer. Raise the temperature to 100 °C while stirring the toluene from time to time. Maintain this temperature for five minutes, then remove the flask and quickly filter the liquid into another flask that has been preheated in the water bath and can then be tightly stoppered. As the second flask cools, sulfur crystals gradually separate from the solution (Figure 159).
WARNING: Throughout the heating process, the Erlenmeyer flask must be connected to an exhaust system to prevent explosive toluene vapors from accumulating in the laboratory.
There is a third method for obtaining crystalline sulfur. Heat sulfur in acetic anhydride. If sulfur is present in excess, it dissolves only partially, the liquid becoming yellow while a globule of molten sulfur remains at the bottom of the test tube. Transfer the upper liquid layer into a warm test tube and allow it to cool. The sulfur then crystallizes as delicate feathery crystals.

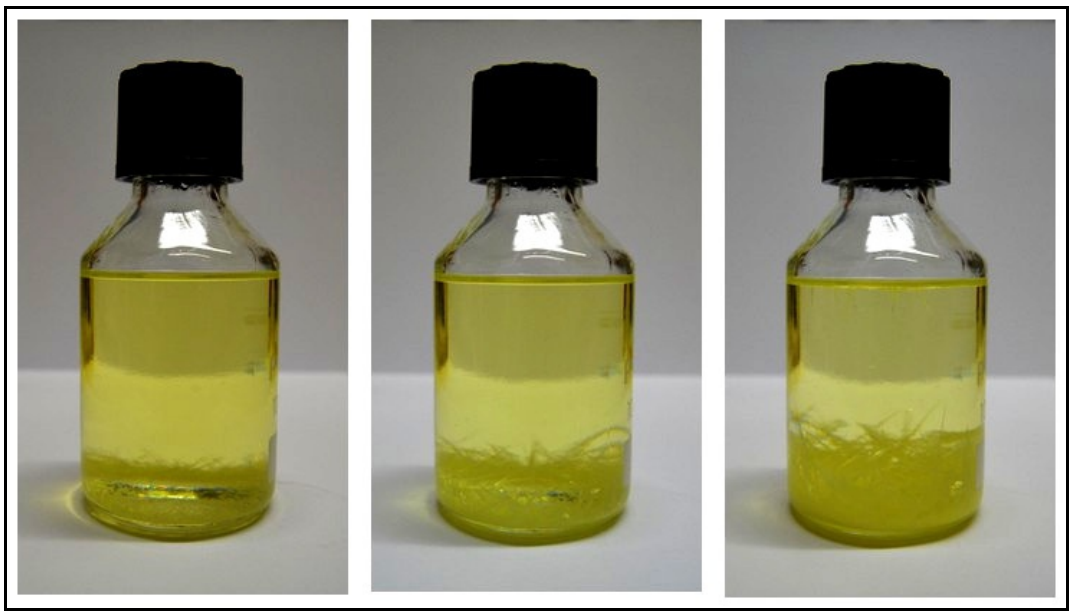


Figure 159

– Heat a small amount of flowers of sulfur in a sodium hydroxide solution. The solution rapidly turns yellow and then brown. A complex mixture of sodium hydrosulfide (NaHS), sodium thiosulfate, and sodium polysulfides has formed.
The same type of reaction can be obtained at room temperature with aqueous ammonia, but in that case the sulfur must be allowed to digest in a translucent polyethylene bottle for at least three weeks, with daily shaking. The liquid gradually acquires a yellowish-red color.
Place a few drops of this liquid into a freshly prepared aqueous lead acetate solution. A brick-orange precipitate forms and settles rather quickly to the bottom of the test tube. In another identical lead acetate solution, add a few drops of ammonium sulfide. A black precipitate is obtained. In a third identical lead acetate solution, add

a few drops of aqueous ammonia. A white precipitate forms. If a small amount of hydrogen peroxide is added to the brownish-red sulfur-in-ammonia solution, the liquid becomes colorless, warms up, and releases ammonia.

– Heat under reflux equal quantities of sulfur and calcium hydroxide in water for one hour (that is, using a vertical condenser mounted above the reaction flask). The liquid becomes increasingly brownish red. Filter it. The filtrate contains calcium pentasulfide (CaS_5). If the boiling time had been shorter, calcium disulfide (CaS_2) would have been obtained instead. The experiment need not end there. After allowing the solution to settle and filtering it, slowly pour the liquid into a large separatory funnel—preferably cooled to about –10°C—containing slightly diluted hydrochloric acid. Shake continuously while pouring. A yellowish-white sulfur emulsion forms together with yellow oily droplets that collect at the bottom of the funnel. This oily phase is hydrogen disulfide or disulfane (H_2S_2), which has a very pronounced hydrogen sulfide odor.
It is essential to proceed exactly as described because H_2S_2 is stable in acids but decomposes in the presence of calcium sulfide. That is precisely what would occur if, contrary to these instructions, hydrochloric acid were poured into the polysulfide solution instead.
Hydrogen disulfide is decomposed by manganese dioxide, sulfides, sugar, or starch. It is also decomposed explosively by alkaline water.

– Sulfur dissolves in a hot aqueous borax solution. This can easily be demonstrated by boiling flowers of sulfur for some time in such a solution. The liquid gradually acquires a yellowish-green color.

– Heat flowers of sulfur in concentrated nitric acid in a large flask (there is a risk that the reaction may run out of control). Red nitrous fumes are evolved, and sulfuric acid is formed. Its presence can subsequently be demonstrated by measuring the pH and by adding a barium chloride solution. With fuming nitric acid, the reaction already takes place at room temperature.

– As previously noted, sulfur dioxide is readily prepared by heating sulfur in concentrated sulfuric acid.

– Boil sulfur in water containing copper(II) oxide. Copper sulfide precipitates, while blue copper(II) sulfate remains in solution. The copper sulfide is identified by adding a few drops of hydrochloric acid, which release the characteristic odor of hydrogen sulfide.

– Pour several centimeters of 33% hydrogen peroxide into a large test tube containing a piece of black selenium about the size of half a pea, broken into small fragments. Heat the test tube in a boiling water bath, then stop heating. Numerous small bubbles appear and then gradually cease to form. Heat the water bath again and repeat the process several times. The selenium slowly decreases in volume until it has completely disappeared, while the contents of the test tube acquire an

unpleasant odor. Selenic acid has formed. Its presence can be demonstrated by adding a potassium bromide solution after the liquid has cooled. A yellow color appears immediately, then the solution gradually begins to foam. A faint reddish cloud fills the upper part of the test tube, and the characteristic odor of bromine becomes noticeable. Eventually, however, the solution loses its color and becomes colorless again.

Selenium

– When heated in concentrated sulfuric acid, selenium turns the acid green, the color rapidly changing from emerald green to spinach green while abundant sulfur trioxide is evolved. In fact, no true sulfate is formed, but rather a complex mixture of unstable selenosulfates and mixed oxides. Allow the mixture to cool, then pour it into water. The water immediately becomes red-orange because of the formation of red selenium. The addition of concentrated aqueous ammonia produces no further color change. If the original red solution is boiled, it gradually loses its color and becomes almost colorless, although still retaining a faint bluish tint. If, however, a few drops of hydrogen peroxide are added before boiling, the solution becomes completely colorless rather quickly.
To avoid possible splashing of sulfuric acid while heating the selenium, it is advisable to use a small flask with a long, narrow neck.

– Selenium does not react with nitric acid in the cold, but when heated it evolves abundant reddish-brown fumes. Heat selenium in nitric acid, then allow the solution to cool and evaporate. Crystallized hydrated selenous acid is obtained. The same product may also be prepared by using aqua regia instead of nitric acid. Selenous acid dissolves readily in water. This colorless solution precipitates red selenium (Figure 160) when brought into contact with zinc and decolorizes an aqueous potassium permanganate solution.

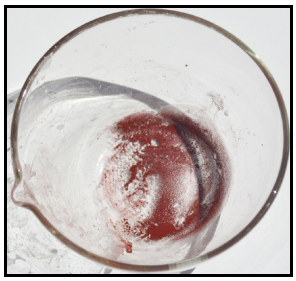


Figure 160

– Pour equal volumes of sulfuric acid and nitric acid into a 100 mL flask, then add a pinch of black selenium. Heat. Brown fumes appear, and the liquid foams vigorously. Reduce the heating and, separately, prepare a hot solution of hydroquinone in sulfuric acid. When foaming has ceased, add the contents of the flask drop by drop to the hydroquinone solution. The liquid then develops a greenish-brown color which, upon dilution, appears rather red.

– Heat selenium with a small amount of potassium hydroxide and a few drops of water. Potassium selenide is formed. Upon addition of water, a red solution is immediately obtained which deposits red selenium when a little hydrochloric acid is added.

Phosphorus

– Place yellow phosphorus in a silver nitrate solution and heat. The liquid turns black and becomes acidic owing to the formation of metallic silver and nitric acid.

– Place 50 mL of water and approximately 0.5 cm^3 of yellow phosphorus in a narrow-necked 100 mL flask. Then add flowers of sulfur in a volume three to four times greater than that of the phosphorus. Place the flask on a magnetic stirrer, which will keep the sulfur at the bottom, and heat to approximately 60–70°C. The liquid gradually clears as the sulfur combines with the phosphorus to form a foul-smelling yellowish liquid that collects around the stirring bar. This is phosphorus monosulfide. Upon standing, it rapidly deteriorates on contact with air and water, becoming milky.

– Place a few small fragments of yellow phosphorus and approximately 25 mL of water in a 100 mL flask. Then add approximately 20 mL of sulfuric acid. The temperature rises. If necessary, heat gently until the phosphorus melts. Next, drop a piece of zinc into the flask. The hydrogen evolved has the strong garlic odor characteristic of impure phosphine, and the phosphorus gradually disappears. Carry out this experiment outdoors or under very efficient ventilation.

– Place small fragments of yellow phosphorus in a copper sulfate solution and heat gently. The surface of the phosphorus soon becomes red because of the deposition of metallic copper, while the liquid, now strongly acidic, contains phosphoric acid together with sulfuric acid.

– Use a 300 to 400 mL ground-glass Erlenmeyer flask surmounted by either a large bulb (300 to 500 mL) or a long empty tube (similar to a distillation column about 40 cm long), the whole assembly being fitted with a gas outlet tube. Place a few small pieces of phosphorus in about 2 cm of water. Bring the water briefly to a boil, then stop heating and darken the room. A "smoke" spreads throughout the apparatus, and a pale green spectral glow appears. When the glow disappears, it is sufficient to heat the liquid gently again. This glow is produced by the phosphorescence of minute particles of phosphorus carried upward by the water vapor. The phenomenon is less conspicuous if the Erlenmeyer flask is not prolonged by a naturally cooled bulb or tube. In that case, it is preferable to use a much larger Erlenmeyer flask (about 5 L) heated on a hot plate. As a reminder, this experiment has already been described in a slightly different form on page 154 (Figure 74).

– The following reaction belongs in this chapter even though, strictly speaking, no external heating is normally required. Place 15 g of red phosphorus in a flask of at least 1 L capacity. Slowly add 100 mL of concentrated nitric acid diluted to half strength. The reaction begins at room temperature, foams vigorously, and may even run out of control. To moderate it, the flask may be surrounded with crushed ice. Toxic gases are evolved, together with nitric acid vapor, which condenses back into the flask by means of the vertical reflux condenser fitted above it. If foaming ceases

while phosphorus still remains, add more nitric acid. Conversely, if nitric acid is in excess, add more phosphorus. In the end, only syrupy phosphoric acid remains.

Boron

– Place a small piece of boron in a test tube and cover it with 1 or 2 cm of concentrated nitric acid. Nothing happens. Heat. The liquid immediately turns yellow and then red, while abundant reddish fumes are evolved. Boric acid is formed during this reaction.

– Hold a test tube vertically and heat about 2 cm^3 of fuming nitric acid. Then drop in a small piece of boron. Although this reaction is generally described as being very vigorous, I did not find it to present any excessive danger.
If the experiment is carried out with boron powder while the nitric acid is heated in a test tube, small flames may occasionally be observed.

14.3 Reactions with Halogens and Halides

– Place a small quantity of nitric acid in a 100 mL ground-glass flask and heat it. When the acid is moderately hot, add iodine crystals and fit the flask with a reflux condenser. Heat somewhat more strongly. Nitrous fumes gradually escape from the flask, while iodine vapors condense. Continue heating gently. The color of the vapors changes and, little by little, the evolution of iodine ceases. Upon cooling, white crystals can be seen deposited in the coolest parts of the apparatus. If desired, the entire liquid may be evaporated to obtain a larger quantity of crystals. These are crystals of iodic acid (HIO_3).

– Place a small amount of iron powder and water in a small Kjeldahl flask and heat. Then add iodine. The liquid rapidly turns green and then brown. Allow it to settle. An iron iodide solution is thus obtained.
The same reaction may also be carried out at room temperature, but it requires several days. In that case, mix the iodine and iron with a little water. After first becoming brown, the liquid gradually decolorizes over the following days. The green color of the iodide is visible only if too much water has not been added.

– Place one part iodine, one part potassium chlorate, and five parts water in a short-necked flask fitted with a vertical condenser, the upper end of which is connected to an exhaust system. The total volume of these substances should not exceed one-third of the capacity of the flask. Some authors recommend adding a few drops of nitric acid, but I did not find this really necessary. Heat slowly until iodine vapor begins to fill the flask. The body of the flask, as well as part of the condenser, soon becomes coated with a layer of iodine. At first the flask appears completely

violet, almost black, but it gradually becomes lighter and finally colorless, while a brown liquid begins to run slowly from the condenser where part of the iodine has condensed. Continue heating until most of the iodine has disappeared, then transfer the liquid from the flask into a tightly stoppered bottle and allow it to cool. White crystals gradually separate. They consist of iodic acid (HIO_3). The supernatant liquid itself contains a large amount of dissolved iodic acid, as can easily be demonstrated with pH indicator paper.
If a small amount of this solution is treated with sulfurous acid added very gradually, iodine is liberated. If more sulfurous acid is added, the brown color disappears because hydriodic acid and sulfuric acid are then formed. If hydrochloric acid is subsequently added, the brown color reappears.

– Add nitric acid to an iodide solution and heat. Iodine is liberated.

– Prepare a fairly concentrated citric acid solution, then add a moderate amount of potassium permanganate solution, followed by a little bromine water. Heat slowly. The solution passes through several colors before finally becoming completely clear. Vapors of bromoaceton are then evolved, recognizable by their very characteristic odor.

– Place a small amount of cellulose, in the form of cotton wool or absorbent cotton (the principal constituent of sawdust), in a flask. Add a generous quantity of chlorine water and heat. The cellulose is attacked, and carbon dioxide is formed.

– Place a mixture of carbon disulfide and bleach in a flask and heat. Connect the flask to a gas-washing bottle containing limewater. Carbon dioxide is evolved.

14.4 Reactions with Mineral Acids or Mineral Salts

Mineral Acids

– Place a piece of neutral litmus paper in a flask containing a saturated boric acid solution. It turns slightly red. Remove the paper and heat the solution. Immerse another piece of litmus paper. This time it turns distinctly red.

– Add a few drops of hydrogen peroxide to a small quantity of hydrobromic acid solution. The liquid slowly acquires a yellow color. Upon heating, the reaction is accelerated and red bromine vapors are evolved.

- Hydrobromic acid converts metallic peroxides (MnO_2, PbO_2, CrO_3) into bromides with the evolution of reddish-brown fumes. Potassium permanganate behaves in the same way. The reaction may begin in the cold, but heating produces a much more obvious result.

– In a test tube, prepare a mixture of nitric acid and sulfuric acid. Add a spatula tip of arsenic trioxide and heat. Brilliant reddish fumes appear, consisting of a mixture of NO_2 and N_2O_4.

– Pour concentrated sulfuric acid onto crystals of tartaric acid. No reaction occurs at first. Upon heating, however, the liquid rapidly changes from colorless to yellow, then brown, and finally black, while sulfur dioxide is evolved. After the sulfur dioxide has been expelled from the flask, a caramelized sugar odor remains.

- Add a little lead dioxide and a manganous salt, such as the chloride or sulfate, to slightly diluted nitric acid. Heat the mixture. The test tube soon develops a brown coloration. This color is caused by potassium permanganate. However, it is not easy to observe because the test tube itself rapidly becomes dark and is covered with numerous small particles.

Sodium, Potassium, and Ammonium Salts

– Prepare a sodium bicarbonate solution and measure its pH. Heat it to boiling. For quite some time, a dense cloud of very fine bubbles rises throughout the liquid. Measure the pH again. The solution has become slightly more alkaline. The change is, however, too small to produce a clearly visible color change with an ordinary acid-base indicator added directly to the solution.

– Place about 2 cm of sodium percarbonate in a test tube and add approximately 4 cm of water. Heat. The liquid begins to foam. A glowing splint inserted into the test tube immediately reignites, demonstrating the evolution of oxygen. In fact, sodium percarbonate decomposes into its two constituents: hydrogen peroxide, which in turn decomposes into oxygen, and a strongly alkaline sodium carbonate solution.

– Boil an alkali sulfite solution. First demonstrate that it releases sulfur dioxide upon addition of sulfuric acid without leaving any precipitate. Once the solution has begun to boil, add a small amount of sulfur and stir. The sulfur gradually disappears, although not completely. Filter the solution and allow it to cool. This solution now reacts with sulfuric acid to release sulfur dioxide while simultaneously producing a heavy sulfur precipitate. Sodium hyposulfite (sodium thiosulfate in modern nomenclature) has in fact been formed.
To make the experiment more instructive, the alkali sulfite may be prepared beforehand. Prepare two identical alkali carbonate solutions. Saturate the first with sulfur dioxide, then mix it with the second. Sodium is generally the preferred alkali metal for preparing the sulfite.

– First grind 25 g of potassium ferrocyanide to a fine powder. Separately, prepare 25 g of concentrated nitric acid diluted with an equal volume of water. Place the ferrocyanide in a 250 mL flask, itself standing in a 1 L beaker filled with ordinary water to serve as a water bath. Set the assembly on an unlit hot plate and pour the

nitric acid onto the ferrocyanide. The reaction begins in the cold. Carbon dioxide, nitrogen, and a small amount of highly toxic cyanogen are evolved, while the liquid gradually develops a coffee-brown color. Once this color has been reached, heat the water bath to boiling. From that point onward, periodically test the liquid in the flask. It is ready when it no longer produces a blue precipitate with an iron(II) sulfate solution but instead a dark green precipitate.
Allow the brown solution to cool. If a few drops are added to a colorless aqueous sulfide solution, even a rather dilute one, a beautiful purple coloration is obtained. Potassium nitroferrocyanide (potassium nitroprusside) is in fact the characteristic reagent for sulfides.
Unfortunately, this reagent cannot be stored because it gradually deteriorates on exposure to air and light.

– Heat a potassium ferricyanide solution to which hydrochloric acid has been added. The initially yellow solution gradually changes to the characteristic goose-dropping green color.

– Place a small amount of sodium nitrite in contact with phosphoric acid. Even at room temperature, brilliant reddish fumes are evolved. Upon heating, the nitrite is rapidly destroyed. With nitric acid or sulfuric acid, heating is required. With hydrochloric acid, no reddish fumes are produced, but a complex mixture is most probably formed, including chlorine.

– Add a potassium chromate solution to a sodium nitrite solution. Then add a little nitric acid to the yellow solution. The color changes to orange with a more or less brownish tint. Heat. After becoming distinctly brown, the solution gradually turns blue-green.

– Prepare a concentrated sodium nitrite solution and add an equal volume of concentrated sodium bisulfite solution. The mixture becomes warm. Sodium nitrylsulfonate is formed. Pour this clear solution into a saturated potassium chloride solution and heat. As the solution cools, a white precipitate gradually appears.
The reaction is complex. Potassium imidosulfonate may have formed or, if boiling has been prolonged, sulfamic acid.

– If several different aqueous ammonium salt solutions are boiled and sparingly soluble strontium carbonate is added to each of them, the strontium carbonate displaces ammonia from the various solutions.

– In a test tube, mix a small amount of ammonium nitrate with an excess of concentrated sulfuric acid. Heat. Nitrogen dioxide is soon evolved, coloring the inside of the test tube orange.

– Heat an ammonium chloride solution with a small amount of powdered barium peroxide. Ammonia is evolved and barium chloride is formed, which may

subsequently be identified by reaction with a sulfate solution.

Iron, Zinc, and Nickel Salts

– Boil an iron(III) chloride solution, then add sulfurous acid. Although the liquid remains yellow, testing it with sodium hydroxide solution no longer gives the usual reddish precipitate but instead a dark green, almost black one. The same reaction also occurs in the cold, although much less distinctly.

– Prepare a very dilute iron(III) chloride solution so that it is only faintly yellow. Divide it into two portions and place each in a separate test tube. Add two or three drops of potassium ferrocyanide solution to the first test tube. The characteristic Prussian blue color is obtained. Heat the second test tube. The solution gradually becomes noticeably darker. Divide it into two equal portions. Add a few drops of potassium ferrocyanide solution to the first portion. The same result is obtained as before. Cool the second portion rapidly under running water. As soon as it has become thoroughly cold, add a few drops of potassium ferrocyanide solution. This time the color is no longer blue but rather greenish.

– Carry out the following test with an iron(III) chloride solution: addition of either sodium hydroxide solution or aqueous ammonia produces a brick-red precipitate. Now heat another portion of the same iron(III) chloride solution in a small Erlenmeyer flask. As the temperature rises, the solution becomes darker. When it reaches the boiling point, add a small amount of iron filings and continue boiling for one minute. Pour a little of the liquid into two test tubes and repeat the tests with sodium hydroxide solution and aqueous ammonia. This time, a green precipitate is obtained.

– Add an iron(III) chloride solution to a sodium formate solution (which may be prepared by neutralizing formic acid with sodium hydroxide solution), then heat. A color change occurs and the liquid becomes cloudy. Allow it to settle. A flocculent precipitate of basic iron formate is deposited. Addition of a little hydrochloric acid converts it back into iron(III) chloride.

– Add an aqueous iron(III) chloride solution to an aqueous sodium acetate solution. Nothing appears to happen. Heat. The liquid becomes cloudy and a more reddish flocculent precipitate forms. It disappears upon addition of a little hydrochloric acid.

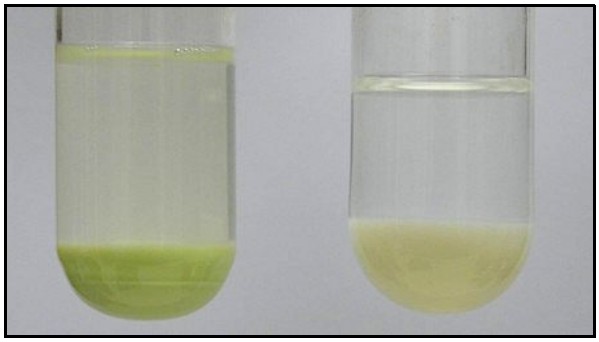


Figure 161

– Fill three test tubes with zinc sulfate solution. To the first, add potassium ferrocyanide solution. An immediate white precipitate forms and gradually

becomes greenish (Figure 161, left). To the second, first acidify the solution with two drops of sulfuric acid, then add potassium ferrocyanide solution. The precipitate is again white but with a faint bluish tint. It does not dissolve upon heating. However, after cooling, it settles as a very white precipitate. To the third, add potassium ferricyanide solution. This time a yellowish precipitate is obtained, which likewise does not dissolve on heating (Figure 161, right).

– Boil a zinc sulfate solution, remove the heat source, and then add a sodium carbonate solution. Abundant foaming occurs, and a white precipitate forms immediately before gradually settling. This precipitate is a basic zinc carbonate formerly used in medicine.

Figure 162

– Place a fairly concentrated nickel sulfate solution in a tall-form beaker and add a small amount of solid zinc chloride. The solution becomes strongly cloudy. Heat it to a gentle boil while partially immersing a well-cleaned long iron nail in the liquid. The solution gradually becomes less cloudy. After only a few minutes, the immersed portion of the nail is covered with a layer of nickel, which is all the more conspicuous because the nail now displays two distinctly different colors (Figure 162).

- Place a small amount of nickel(III) oxide into two test tubes. Pour concentrated hydrochloric acid into the first and concentrated sulfuric acid into the second. At first, nothing appears to happen. Heat both test tubes, then allow them to cool and decant. A green color appears in the hydrochloric acid solution and a yellow color in the sulfuric acid solution. Nitric acid behaves somewhat like hydrochloric acid, although much less vigorously.

- Pour a little hydrochloric acid onto powdered nickel(II) carbonate. A brief reaction occurs, during which carbon dioxide is evolved. Heat gently to complete the reaction. The liquid then becomes clear and develops a beautiful green color. Add aqueous ammonia gradually. At first, the base reacts with the excess acid, producing a small cloud of ammonium chloride. Then, suddenly, once the acid has been completely neutralized, the solution turns a beautiful blue.

- Heat an aqueous solution of nickel sulfate with a little sodium sulfite. The liquid quickly becomes milky with a greenish appearance. Stop heating and add aqueous ammonia. The liquid then becomes blue and transparent. If it is brought back to the boil, the color changes and, little by little, the solution returns to the same milky greenish appearance it had at the beginning.

Copper Salts

- Heat copper(II) oxide (CuO) in a concentrated sodium hydroxide solution. The solution becomes faintly blue.

- Heat copper(II) oxide (CuO) in a solution of ammonium iron(II) sulfate. The color of the solution quickly changes to a dirty yellow.

- Dissolve 50 g of copper acetate in boiling water, then add a concentrated glucose solution while maintaining the temperature close to 100 °C. The liquid becomes greenish, then dirty yellow, and finally brown or brick-red. Allow it to settle. The red precipitate that forms is cuprous oxide (Cu_2O).

- Boil 250 mL of water to expel all dissolved carbon dioxide, then add 50 g of copper sulfate followed by 15 g of glucose. Bring the mixture back to a gentle boil and add 20 g of sodium hydroxide dissolved in 50 to 60 mL of water. Since the reaction is vigorous, it is preferable to use a large round-bottom flask rather than an Erlenmeyer flask whose sides taper inward. During the reaction, a yellow-green-blue precipitate first appears and rapidly turns brick red. Once the lumps have disappeared, add acetic acid until the solution is distinctly acidic, then allow it to settle. The deposit consists of cuprous oxide (Cu_2O). If it is to be recovered, it must be washed several times, allowing it to settle after each washing until the liquid remains perfectly colorless. Placed in sulfuric acid, this precipitate soon colors the liquid blue.

- Add a little dilute potassium hydroxide solution to a dextrin solution, then gradually add a solution of copper sulfate. The mixture develops a beautiful blue color. If it is heated to boiling, the color changes to olive green, then brown and, finally, upon settling, red cuprous oxide is deposited.

- Add an aqueous sodium hydroxide solution to an aqueous copper sulfate solution. A copper hydroxide precipitate forms. Mix well, then carefully pour chlorine water over the mixture until the precipitate becomes green. Heat to boiling. At that point, the precipitate turns black (CuO) and rapidly settles to the bottom of the test tube. Decant the excess liquid and add a little hydrochloric acid. A beautiful green solution is obtained. It is then sufficient to boil the solution and allow it to crystallize in order to recover the salt thus formed.

- Add a copper sulfate solution to a fairly concentrated sodium sulfite solution. A green precipitate of complex composition is obtained. When heated, it becomes brownish-yellow and then black. One or two drops of hydrochloric acid transform it into a greenish liquid.

- Certain carbonates produce a precipitate in a copper(II) sulfate solution, whether at room temperature or upon heating. This may be demonstrated using sodium carbonate, ammonium carbonate, magnesium carbonate, or barium carbonate.

- Pour a sodium nitrite solution into a copper sulfate solution. The solution immediately turns green. If it is then heated, a precipitate forms.

- Heat a copper sulfate solution to which a few drops of sulfuric acid have been added. Once it reaches the boil, add a sodium hyposulfite (thiosulfate) solution. The mixture becomes green, then cloudy, turns yellow, then brown, and finally black. A precipitate of copper sulfide has formed.

- In a flask, mix approximately equal quantities of copper sulfate and sodium hyposulfite. Add enough water to dissolve both salts completely. The solution takes on a dirty green color. Heat it. Gradually, it turns brown and then black as a copper sulfide forms and adheres to the hottest parts of the vessel. This deposit can easily be removed with aqua regia. If the solution is not heated, a light yellow precipitate settles overnight.

- Add a sodium hyposulfite solution to a copper(II) acetate solution. The liquid becomes cloudy and bluish-white. Heat it almost to boiling. After a short time, the solution rather suddenly turns a characteristic goose-dropping green, then gradually darkens until it becomes brown and finally completely black. Stop heating. A black flocculent precipitate rapidly settles to the bottom. Recover it. When cold, it is unaffected by hydrochloric and sulfuric acids. Nitric acid, however, attacks it and, after the evolution of a red gas, the solution is seen to have become a beautiful blue. A small black globule nevertheless remains.

- Prepare a cuprous chloride solution in hydrochloric acid. Place it on a slowly rotating magnetic stirrer and gradually add a moderately concentrated sodium hydroxide solution. Each falling drop produces a yellowish precipitate that immediately disappears because of the stirring. Then, suddenly, the entire liquid fills with a precipitate having the color of burnt sienna. This is a cuprous hydroxide. Evaporate the mixture and then heat it in a test tube. The precipitate crackles and yields cuprous oxide (Cu_2O). React sulfuric acid with this precipitate and compare the result with that obtained by treating CuO with hot sulfuric acid. Two very different sulfates are produced.

- Place a little arsenic trioxide in a small Erlenmeyer flask, pour a copper acetate solution over it, and heat gently for a prolonged period. A green precipitate forms. It is Schweinfurt green, also known as Paris green, formerly used by artists, and corresponding to copper(II) arsenite [$Cu_3(AsO_3)_2$]. It is often confused with Scheele's green, discussed previously, which is a complex compound often identified as copper hydrogen arsenite ($CuHAsO_3$).

- First prepare copper(II) hydroxide by mixing an aqueous copper(II) sulfate solution with an aqueous sodium hydroxide solution. Dilute the mixture with water before heating because the precipitate is very thick and might otherwise be projected out of the flask. Very quickly, the entire liquid turns black owing to the formation of copper oxide. Filter and wash with distilled water to remove any excess

sodium hydroxide or copper sulfate. Cut the filter paper so that only a square about 1 cm on each side coated with the oxide deposit remains. Place this square into a dish containing a very dilute aqueous copper sulfate solution (2 g of salt in 50 mL of water). The black color of the oxide changes to green because an insoluble basic copper sulfate is formed.

- Gradually add an aqueous sulfur dioxide solution to a copper(II) acetate solution. The blue solution gradually becomes cloudy and yellowish-green. Heat it almost to boiling. The solution gradually clears and develops a beautiful emerald-green color. It then darkens and becomes cloudy once again. A fine precipitate is seen to have formed at the bottom of the flask, while tiny particles continually rise and fall through the liquid. Allow the mixture to settle, which occurs very rapidly. At the bottom of a clear light-blue solution, a brick-red precipitate is found. Wash this precipitate quickly and immerse it in a freshly prepared sulfur dioxide solution contained in a flask closed with a ground-glass stopper (which could therefore lift if gas is evolved). It takes many days before the precipitate is seen to decrease in volume while the solution gradually turns sky blue.

Magnesium Salts

- Mix, while hot, a magnesium sulfate solution with a neutral sodium carbonate solution. Carbon dioxide is evolved and magnesium carbonate precipitates.

Lead and Tin Salts

- Add concentrated aqueous ammonia to a boiling lead acetate solution. Depending on various operating conditions, either a white or a yellow precipitate of lead oxide or lead hydroxide is obtained.

- Place a strip of zinc into a lead nitrate solution and heat. A basic lead nitrite is formed and the solution becomes yellow.

- In a 100 mL flask, heat lead(II) oxide, commonly known as litharge, with 40 mL of hydrochloric acid until boiling. Continue heating for a short time, then quickly allow the mixture to settle and pour the liquid into a long test tube. The cold walls of the test tube alone are sufficient to precipitate a little white, insoluble lead chloride ($PbCl_2$). Cool the test tube thoroughly and still more $PbCl_2$ precipitates. Finally, add a large quantity of water. Once again, $PbCl_2$ precipitates as large white flakes because its solubility decreases as the hydrochloric acid becomes more dilute.

- Place a spoonful of litharge in a 250 mL flask and add dilute acetic acid. Heat until some unattacked litharge remains (add more if necessary). Allow the solution to cool, then divide it into four portions. React these portions separately with a sodium hydroxide solution, a little well-diluted sulfuric acid, a sodium or potassium

carbonate solution, and carbon dioxide, respectively. In every case, a white precipitate forms. With carbon dioxide, however, the precipitate is not always very convincing. With sodium hydroxide, it dissolves in an excess of the reagent.

- Pour concentrated hydrochloric acid onto a small quantity of red lead (Pb_3O4). A slight reaction is observed. Heat the mixture. Chlorine is evolved while lead chloride is simultaneously formed.

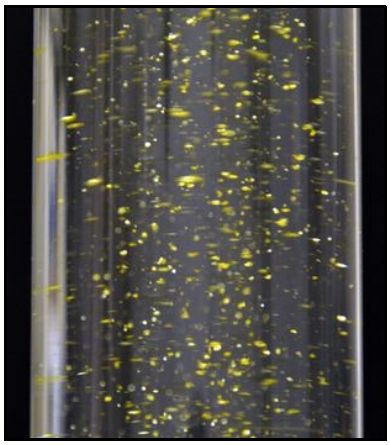


Figure 163

- Prepare a lead acetate solution in a flask or Erlenmeyer flask, then add a potassium iodide solution until a substantial quantity of heavy yellow precipitate has formed. Heat until the precipitate dissolves completely, leaving a clear, colorless solution. Pour this solution into a long tube having an internal diameter of about 20 to 30 mm and allow it to cool slowly. Small, bright yellow crystals gradually appear and rise and fall through the tube, making visible the convection currents produced because the liquid cools more rapidly along the walls than at its center (Figure 163). The process may be accelerated by using a double-walled tube through which cold water or air can circulate, much like a condenser. These crystals differ from the original precipitate, and the experiment may be repeated indefinitely because lead iodide is soluble only in hot water and crystallizes again as the solvent cools.
This experiment has a possible continuation... The filter paper still containing some precipitate is placed in a flask of water, which is once again brought to the boil. The mixture is filtered again and allowed to cool as before. These operations are repeated as many times as necessary until all of the yellow precipitate has dissolved and subsequently crystallized upon cooling. As much water as possible is then removed from the flasks in which the crystals have formed, and the crystals are collected by pouring them into an evaporating dish. Additional liquid is removed with strips of filter paper, after which the crystals are left to dry, if necessary by placing them briefly on a hot plate. Once thoroughly dry, the lead iodide crystals may be recovered. When heated, they become red, but return to yellow upon cooling. If heated more strongly, they blacken and iodine vapors are evolved.

- Prepare a lead acetate solution. Add a freshly prepared (this is important) ammonium thiocarbonate solution. A yellow or red precipitate forms, depending on the concentrations used, and rather quickly turns grayish when stirred. Heat the mixture. Numerous small bubbles are evolved while the liquid becomes black. Allow it to settle. Remove as much of the liquid as possible and add a few drops of hydrochloric acid. The black precipitate foams briefly. From the odor of hydrogen sulfide that is evolved and from the grayish-white grains deposited on the walls of the test tube, it may be concluded that the black precipitate was lead sulfide. The experiment may also be carried out starting from a lead nitrate solution.

- Place a small quantity of anhydrous tin(IV) chloride (stannic chloride) in a porcelain dish and moisten it with turpentine. Sometimes the reaction, which produces dense white fumes, starts spontaneously. At other times, slight heating is required.

- Begin by adding an excess of aqueous ammonia to a tin(II) chloride (stannous chloride) solution. A yellow precipitate forms. Mix it thoroughly and allow it to settle. Decant the supernatant liquid, wash the precipitate with distilled water, then heat it in a glass dish. Where the flame is hottest, the precipitate becomes black, while along the raised edges of the dish a brick-red tin oxide is formed.

Manganese Salts, Manganates and Permanganate

- It is well known that manganese dioxide produces chlorine when heated with hydrochloric acid and oxygen when heated with sulfuric acid. It also produces carbon dioxide when heated with oxalic acid. The initially brown solution finally becomes completely clear. Manganese oxalate has been formed. An ammonium oxalate solution to which a few drops of sulfuric acid have been added produces the same evolution of carbon dioxide.

- Dissolve 10 g of potassium hydroxide in a very small quantity of water, then add 7 g of potassium chlorate and 8 g of manganese dioxide. Heat gently. At first, vigorous bubbling occurs, then gradually subsides as the liquid thickens. Allow the mixture to cool, dilute it with water, and obtain a green solution of potassium manganate in alkaline solution. If very dilute sulfuric acid, carbonated water, or even a little chlorine water is added, the solution is immediately converted into pink to violet permanganate. If air is bubbled through the green solution, it gradually turns reddish-brown and particles of manganese dioxide are deposited.

- In a 100 mL flask, gently heat 20 g of manganese dioxide and 15 g of sulfuric acid to which a few fragments of pumice stone have been added. When the evolution of oxygen has ceased, allow the mixture to cool, dilute it with water and, after settling, obtain a pink solution of manganese sulfate. The evolution of oxygen may be demonstrated by introducing into the neck of the flask a glowing splint that retains only a small red incandescent tip.

- Prepare an aqueous solution of sodium perborate by warming the liquid slightly after adding the salt. This clear, colorless solution is then poured into a pink aqueous solution of manganese chloride. A brown flocculent precipitate of manganese borate immediately forms and, when heated in the solution, rapidly settles.

- Gradually add a sodium cyanide solution to a manganese sulfate solution. A yellowish-red flocculent precipitate forms and eventually disappears completely in a large excess of alkaline cyanide solution. The resulting liquid, initially apricot-colored, rapidly becomes pale yellow. If heated, it turns milky and produces a white precipitate that quickly settles to the bottom. If aqueous ammonia is added

before heating, an apricot-colored precipitate is obtained, which also becomes white after many hours.

- Heat potassium permanganate with phosphoric acid in a porcelain crucible. At first, the mixture foams vigorously. Thereafter, while heating very gently, white vapors are evolved. Finally, a mauve solid is obtained that is much less soluble in water than potassium permanganate.

- Thoroughly grind together 1.7 g of manganese dioxide and 7 g of monoammonium phosphate. Transfer the mixture to a 50 mL crucible and pour 1.2 mL of phosphoric acid over it. Stir with a small glass rod until a paste is obtained, then heat gently. The whole mass melts and becomes black. Its volume increases and bubbles burst at the surface while stirring is continued with the glass rod. When the bubbles display an indigo coloration on their surface, stop heating. If this color does not appear, add a little more phosphate with a spatula. Set the crucible aside. Bring 100 mL of water to a boil in a beaker large enough to receive ce crucible. When the water is hot, pour a small amount of it into the crucible to cool it, then place the crucible in the beaker. A beautiful violet color appears. Continue stirring with the glass rod in order to dissolve as much of the solid as possible, then remove the crucible and allow it to dry and cool. It will become covered with a "violet skin" that can be cleaned off with aqua regia. In the beaker, the violet pigment slowly settles. It is a manganese ammonium pyrophosphate known as manganese violet (Figure 164). The contents of the beaker may immediately be poured into an evaporating dish, the water decanted, the residue allowed to dry, and the dry pigment recovered. It should be noted that, besides the violet pigment, the decanted water acquires a pink coloration due to a small amount of potassium permanganate.

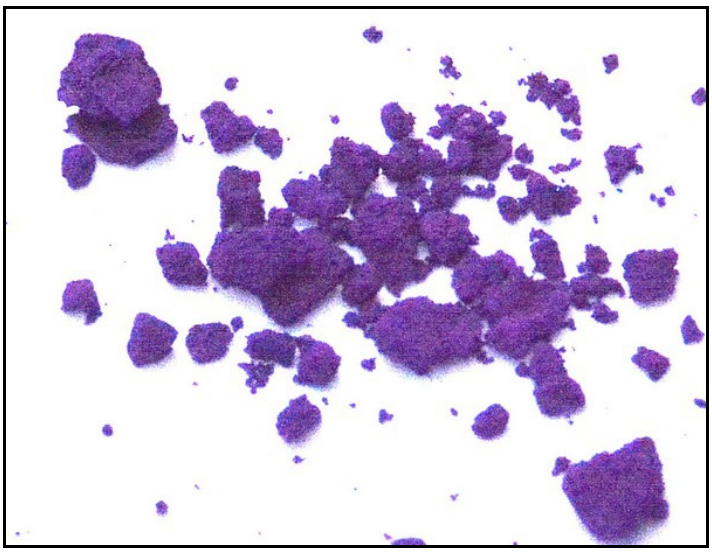


Figure 164

- When a permanganate solution is heated to boiling with an excess of potassium hydroxide or sodium hydroxide, it gradually turns blue, like diluted ink.

- Half-fill a 250 mL flask with distilled water. Add a spatula tip of potassium permanganate and dissolve it. Then alternately add small quantities of ethyl alcohol and sodium hydroxide solution until the liquid develops the beautiful emerald-green color of the manganate ion. Add a few drops of hydrochloric acid. The solution turns reddish-brown. Heat it. It then becomes completely colorless through the formation of manganese chloride. The same reaction occurs if sodium hyposulfite (thiosulfate) is used instead of alcohol.

- Add one drop of glycerol to a warm, slightly acidified permanganate solution. The liquid first turns brown and then becomes colorless. Formic acid is formed.

- Add a substantial quantity of glucose to a dilute potassium permanganate solution whose violet color is clearly visible. Heat the mixture. The color changes, becoming brown (sometimes passing through green and yellow) and finally black. Manganese dioxide (MnO_2) is eventually deposited.

- Place a transparent violet potassium permanganate solution into two small Erlenmeyer flasks. Add a little powdered citric acid to the first and powdered tartaric acid to the second. Even at room temperature, the solution containing tartaric acid changes color slightly. Heat both flasks. Their color soon changes to ruby red, then yellowish-brown and, finally, colorless.
Repeat the same experiment after first adding a little sodium hydroxide solution. This time, with tartaric acid, the color rapidly changes to emerald green, then to brown, and finally deposits manganese oxide. With citric acid, on the other hand, the reaction takes longer and, after becoming emerald green, the solution turns dirty green and retains that color long after reaching the boiling point. If allowed to settle, however, a layer of manganese oxide is observed to fall to the bottom, leaving a green solution.

- Prepare two aqueous solutions. The first contains a small amount of potassium permanganate and the second contains five to six times as much citric acid. Once both substances have dissolved, pour one solution into the other at room temperature. Nothing appears to happen. In fact, the reaction is very slow in the cold. To observe it more easily, simply heat the mixture gradually. The violet solution then turns wine red, then gradually yellow, and finally colorless (Figure 165)

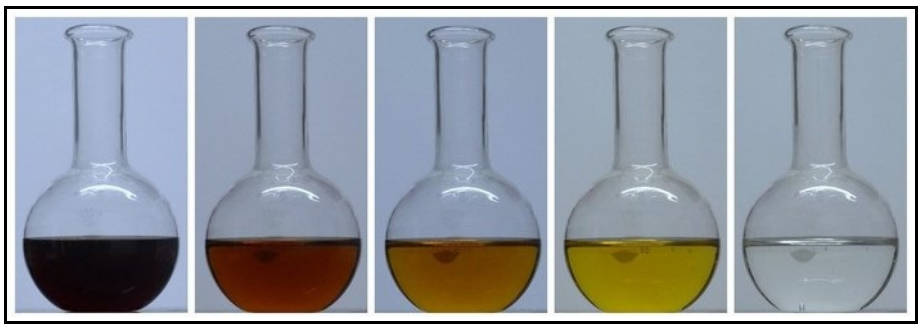


Figure 165

- Prepare a very dark potassium permanganate solution in a flask so concentrated that it is no longer transparent. Carefully pour a moderately concentrated tartaric acid solution over it. Nothing happens. Keeping the total volume below one-third of the flask capacity, heat the mixture. Above about 50°C, small bubbles appear. The gas is passed into a flask containing limewater, where it forms a white precipitate. It is therefore carbon dioxide. Gradually, the liquid becomes completely black. Stop heating and allow it to settle. The liquid then clears while black manganese dioxide is deposited.
If a little dilute sulfuric acid had been added at the beginning, the reaction would have been more vigorous because the evolution of carbon dioxide would have caused the liquid to foam more strongly.
This experiment may sometimes produce quite different results depending on the concentrations employed. For example, if the permanganate solution is not sufficiently concentrated, the mixture becomes completely colorless at about 50°C, and the MnO_2 deposit may be so slight that it passes unnoticed.

- Pour approximately 30 mL of a very dilute (pale pink) aqueous permanganate solution into each of two beakers. Place approximately 2 cm^3 of potassium nitrate powder into each of two separate test tubes. Dissolve the contents of the first test tube in a little water and pour the solution into the first beaker. Nothing happens. Heat the potassium nitrate in the second test tube until it has completely melted and a few bubbles appear. Allow it to cool, dissolve it in a little water, then pour this solution into the second beaker. A color change, or even complete decolorization, is observed. Upon heating, the potassium nitrate has indeed been converted into potassium nitrite. To produce a convincing demonstration, this experiment must be carried out with a relatively large quantity of nitrate compared with the amount of permanganate.

- Add two drops of mercury to a fairly concentrated potassium permanganate solution and heat gently to avoid excessive bumping. After some time, the solution rather suddenly turns dirty brown. Stop heating and allow it to settle. A black deposit collects at the bottom, leaving a colorless liquid. This liquid is strongly alkaline. It is a potassium hydroxide solution. The dark deposit consists of manganese dioxide. Mercury oxide has also been formed according to the following equation: $2KMnO_4 + 3Hg + H_2O \rightarrow 3HgO + 2MnO_2 + 2KOH$
The same reaction occurs in the cold, but it is very slow and requires several days before the black deposit becomes clearly visible and the mercury disappears.
If, instead of stopping the heating at the first color change, the operation is continued, the liquid then turns yellow and finally black. This time, black mercurous oxide (Hg_2O) has been formed. Decant the liquid and collect the black powder, placing it into a long test tube that is then heated. The cooler parts of the tube become coated with a thin layer of bright metallic mercury.
As stated above, the reaction proceeds more slowly in the cold, and only HgO is formed, never Hg_2O.

- Place a small quantity of red phosphorus into a potassium permanganate solution

and bring it to a boil. The color changes, becoming dark red. Allow the mixture to settle. A dark red deposit falls to the bottom of the test tube, leaving a strongly decolorized solution.

Chromium Salts and Chromates

- Place a small quantity of green chromium(III) oxide powder into a 100 mL Erlenmeyer flask, then pour concentrated nitric acid over it. Heat for a short time and, after observing that no reaction occurs, add a little powdered potassium chlorate. The color of the liquid immediately changes to yellowish green. A small quantity of this liquid, diluted with water, produces the characteristic yellow color indicating the formation of a chromate. This mixture is therefore suitable for cleaning glassware contaminated with chromium(III) oxide.

- In a long test tube kept cool in its upper part and connected to a wash bottle containing a little water, heat chromium trioxide in concentrated hydrochloric acid moderately. As soon as the liquid appears about to boil, stop heating immediately. A red gas is evolved while leaving red streaks on the cool walls of the test tube. The water in the wash bottle rapidly turns yellow. Chromyl chloride has been formed and reacts with the water to regenerate hydrochloric acid. This experiment should be kept brief in order to avoid certain hazards. See the comments concerning chromyl chloride in Chapter 15.7.

- Place a small quantity of potassium chromate in a test tube and pour a little sulfochromic mixture over it. If the mixture is heated moderately, the liquid becomes deep red and the chromate disappears. Chromyl chloride is formed. Stop heating as soon as the upper part of the test tube begins to turn red because chromyl chloride is highly toxic and extremely reactive. It must therefore be prevented from escaping into the air.

- Prepare a concentrated hydrochloric solution of chromium trioxide and add concentrated sulfuric acid drop by drop while stirring. Chromyl chloride is evolved and the liquid gradually turns green. If the orange hydrochloric solution is left standing without the addition of sulfuric acid, it also eventually becomes green while very slowly evolving gas.

- Pour a small quantity of hydrobromic acid into a test tube and add a few small fragments of chromium trioxide. The liquid becomes orange. If it is heated, however, both the odor and the color developing in the upper part of the test tube reveal that the coloration is due to bromine being evolved, which at first remained dissolved in the solution. On heating to boiling, the evolution of bromine becomes much more apparent.

- Place a few crystals of chromium trioxide in a test tube. Pour an excess of concentrated ammonia over them and heat. The solution becomes yellow, as do the

chromium trioxide crystals. Unstable ammonium chromate has been formed, which subsequently tends to convert into dichromate.

- Warm a small quantity of sodium perborate in water until it dissolves. Separately, prepare a little orange chromic acid by dissolving a very small amount of chromium(VI) oxide in water. If the perborate solution is poured into the acid, an immediately very dark brown liquid is obtained. Conversely, if the acid is gradually poured into the perborate solution, accompanied by a vigorous evolution of gas, the liquid gradually changes from lemon yellow to brown. Perchromic acid has thus been formed.

- Heat a violet chromium sulfate solution. The color slowly changes to green while the pH becomes more acidic. On cooling, the original color reappears. The same color change may be observed by heating violet crystals.

- To a bluish-green chromium sulfate solution, add dilute ammonia and a little hydrogen peroxide. The solution changes from milky green to brown. Heat it. As oxygen is gradually evolved, the solution acquires a beautiful yellow color. Ammonium chromate has been formed.

- Heat green or mauve chromium sulfate in concentrated sulfuric acid. The color gradually changes, finally becoming yellow and then pinkish red.

- Pour a little chromium sulfate solution into a test tube. Add a little sodium hydroxide solution followed by one or two drops of hydrogen peroxide. Heat the mixture. The blue to bluish-green liquid becomes orange and then yellow.

- If solid borax is heated with violet chromium sulfate, a green bead is obtained which, when dissolved in water, gives a greenish-blue solution.

- Into three test tubes, each containing the same quantity of potassium chromate solution, pour equal amounts of lead acetate solution. Three yellow precipitates are thus obtained. Add a little potassium hydroxide solution to the first, a little hydrochloric acid to the second, and a little nitric acid to the third. In all three cases, the precipitate disappears, leaving a clear yellow solution. The shades, however, are different. With potassium hydroxide, a light canary-yellow solution is obtained. With either acid, the color shifts toward orange. Next, add a little solid potassium chromate to each test tube and heat. Nothing very noticeable occurs in the alkaline solution, the nitric acid solution turns distinctly red, whereas the hydrochloric acid solution first becomes red and then gradually changes to an olive-yellow color.

- Place a small quantity of solid potassium chromate in a test tube and pour concentrated hydrochloric acid over it. The liquid rapidly becomes reddish brown. Heat to boiling and continue heating. The liquid eventually turns green.

- Add an excess of concentrated hydrochloric acid to a concentrated potassium

dichromate solution. The liquid changes color, becoming dark red. Bring it to a boil. The solution gradually becomes dark green owing to the formation of chromium(III) chloride. The resulting solution is impure because it also contains potassium chloride. A strong chlorine odor is noticed, although no visible gas evolution occurs. One author recommends heating three parts of potassium dichromate with four parts of concentrated hydrochloric acid and a little water. When the chlorine odor becomes pronounced, pour the liquid into an evaporating dish and allow it to crystallize. When these crystals are mixed with ether, they are capable of reacting with ammonia gas to produce potassium amidochromate in the form of beautiful red prisms.
Here is a variation of this experiment that produces very different results. Mix 115 mL of 36% hydrochloric acid with 100 mL of water preheated to about 50°C. Add 100 g of potassium dichromate and heat until it has dissolved. The solution becomes intensely orange. A solution of potassium chlorodichromate ($KCrO_3Cl$) has thus been prepared.
WARNING: if the acid is too concentrated, chlorine will be formed. As soon as vapors begin to appear, stop heating and allow the solution to cool slowly while covering it with plastic film. Filter through a fritted-glass funnel and wash the crystals with a little cold water. About 75 g of potassium chlorochromate are obtained. Place a small quantity in a beaker and pour a little methanol over it. Stand well back, because the material first turns black and then becomes "volcanic."

- Dissolve 19 g of sodium dichromate in 80 mL of water in a tall 500 mL beaker and heat without bringing the solution to a boil. Then add, in small portions, a mixture previously prepared in a porcelain mortar from 50 g of oxalic acid and 23 g of neutral sodium oxalate. Vigorous effervescence occurs owing to the abundant evolution of carbon dioxide. When the entire mixture has been added and the effervescence has ceased, heat to boiling while stirring until the volume has been reduced by half. Pour the remaining liquid into one or more shallow dishes and allow it to crystallize. Mauve crystals of sodium tris(oxalato)chromate(III) are obtained.

- Heat a sodium dichromate solution in a 500 mL wide-neck flask. When it reaches the boiling point, add powdered sodium carbonate in small successive portions. Stop adding it as soon as gas evolution ceases. The dichromate has now been converted into golden-yellow neutral chromate.

- Pour an aqueous potassium dichromate solution into a large test tube. Then add an aqueous silver nitrate solution until a fairly dark brick-red precipitate is obtained. Divide the mixture into several test tubes.
Heat one portion. The liquid becomes lighter in color and turns orange. Add ammonia. Depending on the concentrations employed, the solution becomes either a beautiful orange or lemon yellow.
In another portion, add ammonia directly without heating. Here again the liquid becomes orange or lemon yellow owing to the formation of chromate. The same result is obtained if nitric acid or hydrochloric acid is used instead of ammonia.

- Add powdered magnesium carbonate to a concentrated orange potassium dichromate solution and heat gently. Vigorous effervescence occurs and the solution becomes increasingly yellow. The reaction is complex and is believed to produce $K_2CrO_4 + MgCrO_4 + 2H_2O$.

- Heat a potassium dichromate solution to which concentrated hydrochloric acid has been added. The color gradually changes from orange to mahogany brown. Potassium chlorochromate has been formed.

- Pour an aqueous potassium dichromate solution into a small Erlenmeyer flask, then add concentrated hydrochloric acid, followed by a little ethyl alcohol. Even at room temperature, the color changes fairly rapidly from orange to brown and finally to a dull green. Heat moderately. The color continues to change until it finally becomes emerald green, while the easily recognizable odor of acetaldehyde (ethanal) is perceived. Chromium(II) chloride has been formed.

- Add a little lactic acid to an orange potassium dichromate solution. The solution soon becomes darker. Heat it. The color becomes progressively darker, finally tending toward a very dark bluish gray.

- Add a little solid oxalic acid to a potassium dichromate solution and heat. The color of the liquid rapidly becomes darker.

- Add a little formalin to a potassium dichromate solution. At first nothing happens, but the color slowly becomes darker. Heat the solution. It gradually darkens further and becomes cloudy with a brick-red coloration. Allow it to settle for a few minutes, decant the supernatant liquid, then add a little water together with two or three drops of sulfuric acid. Heat once more. A beautiful teal-blue solution of chromium sulfate is obtained.

- Heat black, insoluble iron chromate in concentrated hydrochloric acid for several minutes while collecting the evolved gas in a wash bottle containing a little water (a safety tube fitted with a large bulb should be provided). After settling, a yellow solution is obtained. This yellow solution gives a beautiful blue coloration with potassium ferrocyanide solution, a beautiful red coloration with sodium thiocyanate solution, and a white precipitate with ammonium sulfide solution.

- Using the same insoluble iron chromate, replace hydrochloric acid with sulfuric acid and heat for a prolonged period. The considerable bumping of the acid is partly controlled by adding a few fragments of pumice stone. After cooling and settling, a green solution is obtained. Dilute it and allow it to react with ammonium sulfide. A white gelatinous precipitate is formed. If the green solution is instead allowed to react with sodium thiocyanate solution, a faint yellow coloration together with gas evolution is observed. When reacted with potassium ferrocyanide solution, a white precipitate first forms, begins to dissolve, and then persists.

- Prepare a yellow precipitate of neutral lead chromate by reacting an aqueous lead acetate solution with an aqueous potassium chromate solution. Wash the precipitate with water and suspend it again in water. Using a pipette, transfer a small quantity into another test tube and pour over it a mixture of ethyl alcohol and hydrochloric acid. A slight decolorization is observed. Heat the mixture. The liquid becomes transparent and develops a beautiful light-green color owing to the formation of chromium(III) chloride.
The yellow precipitate may also be mixed with a potassium hydroxide solution. It dissolves, producing a clear solution of a beautiful canary-yellow color.

- Prepare a saturated aqueous solution of ordinary alum and another of chrome alum. The first is colorless and the second is blue. Mix them in equal proportions. The resulting solution is blue. Heat it in an evaporating dish. The liquid becomes emerald green, and the crystals deposited are of the same color.

- Place a fairly concentrated mauve-blue solution of chrome alum into a test tube. Add a little sodium hydroxide solution. A green precipitate forms. Stir it, then add two drops of hydrogen peroxide and stir again. The mixture develops a dull olive-green color. Heat it, and the solution becomes canary yellow [chromium(VI)]. Continue heating while stirring to expel as much oxygen as possible, then add a few drops of sulfuric acid. Depending on the concentrations employed, a transparent reddish or green solution is obtained.
Add a layer of ether about 2 cm deep and then allow two drops of hydrogen peroxide to fall into the tube. A blue-violet upper layer forms above a green lower layer.

- Add a little sodium phosphate to an aqueous chrome alum solution. A bulky green precipitate forms. If a strong acid such as sulfuric acid, nitric acid, or hydrochloric acid is then added, a clear green solution is obtained. These reactions occur even in the cold, but proceed more rapidly with gentle heating.

Cobalt Salts

- Cobalt oxide (Co_3O_4) reacts with hydrochloric acid at room temperature, slowly producing a beautiful blue solution that becomes pink when water is added. The reaction proceeds even more rapidly when heated. The same oxide reacts only slightly with concentrated sulfuric acid in the cold, but on heating it rapidly produces a pink-lilac solution. With nitric acid, no reaction occurs, even on heating.

- Pour a sodium sulfite solution into a hot cobalt chloride solution. A mauve flocculent precipitate of basic cobalt sulfite immediately forms. The addition of a few drops of sulfuric acid causes it to disappear instantly, and the liquid regains its original pink color.

- Add a sodium cyanide solution to a pink cobalt chloride solution. A brown

precipitate immediately forms and gradually becomes lighter in color. Stop adding the sodium cyanide before the liquid has become clear, then divide it into two equal portions.
In the first portion, continue adding sodium cyanide solution until the liquid becomes clear and yellow. Heat it to boiling. Nothing happens.
Heat the second portion directly to boiling. A green flocculent precipitate is formed.

- Bring a pink cobalt chloride solution to a boil. While maintaining boiling, add moderately concentrated ammonia little by little. A blue precipitate first forms, then changes to dull olive green, and finally becomes pink. This precipitate of triammine cobalt chloride ($Co(NH_3)3Cl_3$) settles rather quickly as a cotton-like mass whose surface slowly turns brown. A very similar experiment can be carried out in the gas phase. In this case, begin with a solution of cobalt chloride in amyl alcohol. It is a beautiful blue. Pass thoroughly dry ammonia gas through the solution. It soon changes to a dull olive-green color and then slowly turns pink. The precipitate settles rather quickly as soon as the passage of the gas is stopped.

Figure 166

- Place a small quantity of crystalline cobalt chloride in syrupy phosphoric acid and heat. Blue traces first appear around the crystals, but the entire liquid gradually becomes violet to ruby-red, depending on the amount of crystals initially used. On cooling, it turns pink. Add water, followed by a potassium hydroxide solution. A blue precipitate is obtained which gradually becomes lighter on exposure to air. If ammonia is used instead of potassium hydroxide, either a beautiful deep-blue solution or a pale-blue precipitate is obtained, depending on the quantities employed. If hydrochloric acid is then added to this latter precipitate, the original pink solution is restored (Figure 166).

- Prepare a pink cobalt sulfate solution. Add a sodium bicarbonate solution and heat. A violet cobalt carbonate precipitate forms. Add a few drops of hydrochloric acid. The liquid again becomes transparent and pink because cobalt chloride has now been formed.

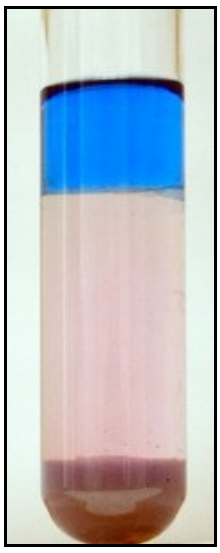


Figure 167

- Fill three test tubes with 3 to 4 cm of a pink aqueous cobalt chloride solution. Into the first, add a few drops of potassium ferrocyanide solution. A green precipitate forms. On heating, it becomes somewhat darker. Into the second, add a few drops of potassium ferricyanide solution. A reddish-brown precipitate forms. On heating, it takes on the color of old wine. Into the third, add a few drops of sodium thiocyanate solution. A lilac precipitate forms. On heating, its color tends toward mauve. Then add a little amyl alcohol followed by ether and shake the tube. A blue upper layer forms without mixing with the rest of the liquid. The precipitate subsequently collects at the bottom. This appearance

may remain essentially unchanged for more than twenty-four hours. Thereafter, the alcohol gradually evaporates, the blue layer decreases accordingly, and the precipitate tends to become lighter in color (Figure 167).

- Place a pink cobalt chloride solution in a beaker resting on a hot plate that is initially switched off. Add a little sodium hydroxide solution without excessive stirring. Two layers form: a pink upper layer and a blue lower layer. Switch on the hot plate. Three layers then appear, from bottom to top: yellowish-brown, pink, and blue (Figure 168).

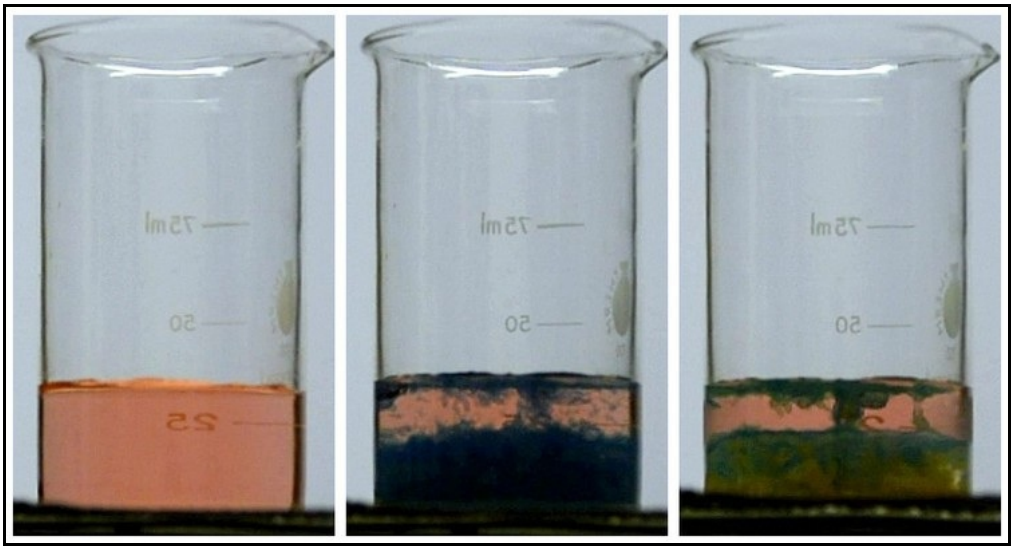


Figure 168

If this experiment is performed on a heated magnetic stirrer, the color changes very rapidly from pink to brown, demonstrating the importance of observing the formation of a precipitate throughout all its stages and at different temperatures. The addition of a little hydrogen peroxide produces abundant foaming, and the precipitate becomes much darker.

- Cobalt chloride dissolves in glycerol when heated. To carry out this experiment, pour 1 or 2 cm of glycerol into a test tube in which a few crystals of cobalt chloride have previously been placed. No dissolution is observed. Heat the test tube slowly. The cobalt chloride then dissolves, forming a blue liquid. On cooling, it becomes carmine pink. I have not been able to verify whether it turns yellow when cooled to a very low temperature.

Molybdenum Salts

- If an aqueous sodium chloride solution is added to an aqueous solution of molybdenum trioxide and the mixture is brought to a boil, cooling produces a white gelatinous precipitate.

- If a yellowish-red iron(III) chloride solution is added to an aqueous solution of molybdenum trioxide, a slight cloudiness appears. On heating, a distinct red precipitate forms and then settles rapidly.

- Dissolve potassium bitartrate in distilled water while heating, then add a little zinc powder. The reaction is slow, but the solution remains colorless. If, however, a little molybdenum trioxide is mixed with the potassium bitartrate beforehand, the addition of zinc to the still-hot solution produces vigorous effervescence, and the liquid first becomes a very dirty, cloudy brown before changing to a clear orange-brown.

- Pour a little aqueous ammonium molybdate solution into a porcelain evaporating dish, then add two or three drops of concentrated sulfuric acid. Heat until the liquid has almost completely evaporated. The walls of the dish become blue.

- Pour an aqueous ammonium molybdate solution into a test tube, then add a few crystals of potassium iodide. Nothing happens. Add a few drops of hydrochloric acid. A yellow-orange color rapidly appears around the crystals and, on heating, the entire solution quickly turns blue. Divide this blue solution into two portions. Add more hydrochloric acid to the first portion and continue heating. Iodine is soon liberated and deposits on the cool walls of the test tube, while the solution gradually changes to a very dark green, almost black. If concentrated ammonia is then added gradually, a yellowish-brown precipitate is obtained. In contrast, if concentrated ammonia is added drop by drop to the second portion, which has been only very slightly acidified, the blue color disappears and the solution becomes cloudy. As the precipitate gradually settles, two differently colored layers are observed: one yellowish-brown and the other slightly greenish.

Titanium Salts

- Heat titanium oxide in concentrated sulfuric acid for 15 to 30 minutes. The resulting yellowish-white syrupy liquid is then poured, with stirring, into water and allowed to cool and settle. Transfer part of the clarified solution into a test tube and gradually add a substantial quantity of either sodium hydroxide solution or ammonia. In both cases, the liquid gradually becomes cloudy. Within a few minutes, the cloudiness gathers into a white flocculent precipitate. If potassium ferrocyanide solution is used instead of these alkaline solutions, the reaction is slower and less obvious. After a considerable time, slight cloudiness appears and the color gradually shifts toward yellowish green. Add a little hydrogen peroxide to the original solution, after dilution with water and cooling. A yellow coloration appears.
All these observations demonstrate that concentrated sulfuric acid does react with titanium oxide when heated, although only to a limited extent.

- Heat titanium dioxide (TiO_2) in hydrochloric acid for a few minutes. Allow the mixture to settle. Add a few drops of hydrogen peroxide to the clear, or partially

clarified, liquid. A yellow coloration appears, indicating that titanium chloride has been formed.

- Mix a little violet titanium chloride solution with powdered salicylic acid and heat. The liquid first becomes dirty yellow before turning onion red.

- Add sulfurous acid to a hydrochloric titanium chloride solution having a mauve color. The solution rapidly turns brown and then becomes lighter. It now contains hyposulfurous acid. If the solution is then heated, it becomes completely white because a milk of sulfur is formed as the result of a reaction between hydrogen sulfide and sulfur dioxide.

Vanadium Salts

- Add an aqueous barium chloride solution to a neutral aqueous ammonium vanadate solution. A white precipitate resembling curdled milk is obtained. On boiling, it becomes slightly yellow. Then add nitric acid drop by drop. After first producing a yellow-orange coloration, the precipitate disappears completely and the liquid becomes almost colorless.

- Mix together two aqueous solutions: one of ammonium vanadate and the other of cobalt nitrate. Then add one drop of nitric acid and bring the mixture to a boil. At first, nothing appears to happen. The solution remains clear and orange in color. Allow it to cool. A red precipitate of cobalt metavanadate then appears

- Place a little red phosphorus into a yellow aqueous solution of vanadium pentoxide and bring it to a boil. The phosphorus disperses into minute particles that color the solution, which may briefly appear bluish. Allow the mixture to cool and settle. The solution has become colorless.

- Vanadium pentoxide reacts with hydrobromic acid solution when heated, producing a yellowish-green liquid.

- Heat an aqueous oxalic acid solution in a flask having a relatively narrow neck. Then gradually add vanadium pentoxide as long as each addition produces foaming. Finally, bring the mixture to a boil and allow it to settle. A beautiful blue solution is obtained, which may be diluted with water. The addition of hydrogen peroxide changes the color first to orange and then to yellow (more rapidly if the solution is heated), whereas the addition of sodium hydroxide solution changes it to red. If a strip of zinc is placed in the blue solution, a succession of colors is observed: orange, blue, green... together with a black deposit. No comparable effect is obtained with a strip of copper or with a few drops of mercury.

- Prepare a mixture of equal parts of aniline and concentrated HCl. The mixture quickly becomes pasty. Bring it into contact with an aqueous solution of vanadium

pentoxide and shake. A dark red liquid is formed. If the pasty mixture is instead brought into contact with an aqueous solution of ammonium vanadate, an emerald-green liquid is obtained, which gradually changes to denim blue. Heating the solutions accelerates and enhances the reactions.

- Place a pea-sized amount of vanadium pentoxide in a 100 mL flask. Pour concentrated ammonia solution over it. A sound similar to that produced when red-hot iron is plunged into water is heard. Heat the flask. Gradually, the liquid becomes milky. The yellow-brown vanadium pentoxide slowly loses its color. Stop heating and filter. The filtrate is colorless. Ammonium vanadate has been formed. Dilute it with a little water and add a few drops of H_2SO_4. The liquid turns canary yellow. Repeat the experiment, but add a few drops of H_2O_2 instead of sulfuric acid. The liquid again becomes yellow, but this color rapidly disappears. If a zinc rod is placed in this solution, nothing happens. However, if the solution is first diluted with water, a yellowish-brown coloration appears very slowly.
If H_2O_2 is added to the ammonium vanadate solution after it has been acidified with H_2SO_4 and has therefore changed from colorless to yellow, the color now turns blood red or even brown. This is a very sensitive reaction.
If this liquid is then heated to boiling, it suddenly appears to become black before changing to a beautiful emerald green.

- Add an aqueous nitric solution of mercuric nitrate to a neutral aqueous solution of ammonium vanadate. A yellow-brown precipitate forms and remains unchanged on boiling. If HNO_3 is then added, the precipitate gradually disappears, the liquid turns green, and reddish-brown nitrogen oxide fumes are evolved.

Mercury, Silver, and Gold Salts

- Boil barium sulfate with mercuric nitrate in hydrochloric acid solution. A yellow basic mercuric sulfate is obtained. This compound was historically known as mineral turbith.

- Start with an aqueous solution of mercury(II) chloride and add a potassium chromate solution. The reaction may begin only after a second or two, producing a reddish precipitate. Boil for one minute, then allow the brick-red precipitate to settle. Pour off most of the liquid and add a few drops of HCl. The precipitate immediately dissolves to give an orange solution which, when diluted with water, becomes yellow again because of the chromate ions.

- In a test tube, react a mercury(II) chloride solution with a potassium carbonate solution. A precipitate forms whose color depends on the amount of carbonate used. Boil the mixture and allow it to cool. Decant the liquid, then heat the precipitate. Depending on the temperature reached, yellow or red colors are obtained, corresponding to the different forms of mercury(II) oxide (yellow and red). If heating is continued, oxygen is released and metallic mercury reforms.

Warning: Mercury vapor is highly toxic. Avoid prolonged heating and stop as soon as a dark purple-to-black coloration appears. This dark color changes again during cooling.
The same experiment may also be carried out with a nitric solution of mercury(II) nitrate.

- Fill two test tubes, one with a mercury(II) chloride solution (prepared by gentle warming) and the other with a mercury(II) nitrate solution. Add sulfurous acid to each. A slight flocculent precipitate may first appear, but it develops into a white or slightly yellowish powder only after heating to boiling. With the nitrate solution, the precipitate gradually turns yellow, and when all the liquid has evaporated, red fumes are observed.

- Pour a mercuric nitrate solution into two separate test tubes. Into the first, add a potassium iodide solution. An orange-red precipitate forms. Heat until the liquid has evaporated. During heating, the precipitate becomes a deeper red. This red mercuric iodide deposits on the walls of the test tube and turns yellow when heated. Into the second test tube, continue adding the potassium iodide solution until the orange-red precipitate disappears. A yellow solution is then obtained. Add a silver nitrate solution. A lemon-yellow precipitate forms. Heat to remove the water. The lemon-yellow precipitate then becomes yellow-brown. Contrary to what is stated in certain publications, I have found that, on cooling, neither precipitate really regains its original color.

- In a test tube, mix a barium chloride solution with a sulfate solution so that a white barium sulfate precipitate is obtained. Transfer this precipitate to a silver nitrate solution and heat. A yellow precipitate is obtained, also referred to by some authors as turbith.

- Heat a small amount of potassium nitrate in hydrochloric acid and, once the mixture has become slightly colored, immerse small fragments of gold leaf in it. The gold "dissolves" because this mixture is a variation of aqua regia.

Antimony and Arsenic Salts

- Add a few crystals of sodium hyposulfite (sodium thiosulfate) to a solution of an antimony salt and heat. A brick-red precipitate is obtained.

- Boil antimony pentasulfide in hydrochloric acid. Hydrogen sulfide is evolved, sulfur is deposited, and a pink solution of impure antimony trichloride remains. This experiment constitutes the first step in the historical preparation of pure antimony trichloride.
Then add a sodium thiosulfate solution to the hydrochloric antimony trichloride solution thus obtained. Nothing happens at first. Heat the mixture. Little by little, the liquid turns yellow and then red. As soon as boiling is reached, stop heating and

allow the mixture to stand. A red precipitate forms. This is antimony vermilion, the amorphous antimony trisulfide Sb_2S_3.

- If solid arsenic trioxide is heated with a small amount of solid potassium nitrate, reddish-brown fumes are evolved. Dilute the residue with water and then add a few drops of silver nitrate solution. A purple to red coloration appears. An arsenate is, in principle, formed. The result, however, did not appear conclusive in my own experiments.

- Place half a teaspoonful of arsenic trioxide in a 250 mL flask and cover it with about 1 cm of concentrated nitric acid. Heat the flask. The liquid turns yellow and then gives off abundant reddish-brown nitrogen oxide fumes. This experiment must therefore be carried out outdoors or under very efficient ventilation. After cooling, a yellow liquid containing arsenic pentoxide (As_2O_5) is obtained. Unlike arsenic trioxide, this compound dissolves readily in water. The solution may be evaporated to recover the crystals.

- Add arsenic trioxide to a concentrated sodium carbonate solution and heat to about 90 °C. The liquid becomes translucent. Sodium arsenite ($NaAsO_2$) and carbon monoxide are formed. Sodium hydroxide may be used instead of sodium carbonate. If a copper sulfate solution is then added to this sodium arsenite solution, a green pigment is produced (See also page 402).

- Add a small amount of arsenic trioxide (arsenious oxide) to an aqueous solution of an alkali carbonate and boil for one minute. Then add a few drops of aqueous silver nitrate solution. A yellow precipitate is obtained, indicating the formation of an arsenite.

Other Salts

- In an Erlenmeyer flask or a flask, mix 1 part borax with 2½ parts water and bring to a boil until everything has dissolved. Allow the solution to stand briefly until it becomes clear. Heat again until the first signs of boiling appear, then add hydrochloric acid while stirring thoroughly until a colored indicator shows that the solution has become slightly acidic. Cool rapidly under running water or in an ice-water bath. Flakes of boric acid appear. Test this boric acid in a watch glass by adding a small amount of alcohol and igniting it. A green flame is produced. It may also be tested with dry turmeric paper.
The same experiment may be carried out by replacing HCl with H_2SO_4. Exercise caution when adding H_2SO_4.

- Prepare an aqueous solution containing a given quantity of barium chloride and, separately, an aqueous solution containing twice its weight of potassium ferrocyanide. Both relatively concentrated solutions are brought to boiling. They are then mixed and allowed to cool and stand. After several hours, beautiful crystals of

barium ferrocyanide, which is only slightly soluble in water, begin to separate.

- Place a small amount of sodium perborate in a test tube containing 4 or 5 cm of water. It will be observed that it does not dissolve. Warm the test tube gently and dissolution then occurs very readily. Pour this solution into a large test tube containing an aqueous barium chloride solution. A grayish-white precipitate of highly toxic barium borate immediately forms and settles rapidly.

- In a flask or Erlenmeyer flask, mix an aqueous potassium chromate solution with an aqueous solution of a neutral cadmium salt. Even at room temperature, the slow formation of a yellow cadmium chromate precipitate is observed. This process is greatly accelerated by heating the flask to the boiling point. Then allow the mixture to stand and decant the liquid. Pour ammonia solution onto the lemon-yellow powder remaining at the bottom of the flask. A perfectly clear yellow solution of ammoniacal cadmium chromate is obtained.

- Prepare a series of test tubes, each containing either an aqueous strontium chloride solution or an aqueous strontium nitrate solution. It will be observed that, at room temperature, a sodium hydroxide solution produces no visible reaction in either solution. At the boiling point, however, a slight cloudiness appears. The same result is obtained if the sodium hydroxide solution is replaced by ammonium hydroxide.
With a potassium chromate solution, nothing appears at room temperature in the strontium chloride solution, whereas a slight cloudiness develops in the strontium nitrate solution. On heating, a white precipitate appears in both solutions and settles rapidly.

- In a large test tube, place a small amount of bismuth(III) oxide, two or three centimeters of water, and a few drops of hydrochloric acid. Heat to gentle boiling. Then add a small amount of potassium iodide. A beautiful coloration ranging from yellow to orange, depending on the concentrations used, is obtained. This coloration does not occur in the absence of bismuth oxide.
The same experiment may be performed using HNO_3 instead of HCl. However, care must be taken because, above a certain concentration, nitric acid alone is capable of liberating iodine from potassium iodide. The experiment is therefore less demonstrative.
Nothing happens if potassium bromide is substituted for potassium iodide.

- Heat a solution of ammonium chloride or ammonium nitrate. When it is almost boiling, add a small amount of lithium carbonate. A strong odor of ammonia is immediately perceived. At the boiling point, lithium carbonate decomposes ammonium salts in solution.

- Pour 1 cm of distilled water into a 100 or 150 mL Erlenmeyer flask, then add two spatula tips of Prussian blue and finally a small spoonful of strontium carbonate. The mixture has a beautiful blue color with undissolved white grains of carbonate. Boil

for two minutes, then filter. The resulting liquid is yellow -because of the strontium ferrocyanide formed.

- Prepare a hot solution of sodium tungstate. Add concentrated nitric acid drop by drop, then wait. A milky precipitate slowly appears. It then increases rapidly, becoming curdy and yellow. Allow it to settle for a short time, pour off the excess liquid, and divide the precipitate, still mixed with a little liquid, into two portions. Add a strong acid such as H_2SO_4 to the first portion. The precipitate does not dissolve and may even become denser and more intensely colored. Add a solution of an alkali hydroxide such as sodium hydroxide to the second portion. The precipitate then dissolves completely.

- Pour a hot sodium tungstate solution into a fairly dilute mercury(II) chloride solution. A yellow precipitate forms. The same result is obtained with a mercurous nitrate solution.

- Place one spatulaful of cerium dioxide (CeO_2), which is a pale yellowish-white powder, in a small Erlenmeyer flask. Pour concentrated sulfuric acid over it and heat. The powder tends to agglomerate and gradually becomes orange-red. At the same time, SO_3 is evolved, making good ventilation essential. After a few minutes, pour the contents into a narrower flask and allow them to settle. The orange powder then becomes canary yellow. It is neutral ceric sulfate. This powder, still impregnated with acid, is soluble in water (ceric sulfate is insoluble in non-acidified water). It first produces an opalescent liquid which gradually clears over the following minutes to give a beautiful transparent yellow solution.
Frémy's *Encyclopedie Chimique* states that an insoluble basic salt is then deposited. In fact, it seems to me that this occurs only when too much water has been added. It is then sufficient to add more acid for the milky liquid to become yellow again.
On the other hand, if the cerium dioxide is boiled from the outset in dilute sulfuric acid, the orange coloration does not appear. Instead, a gas is evolved which, according to this encyclopedia and also to Paul Pascal's treatise, is ozonized oxygen. A mixture of ceric sulfate and cerous-ceric sulfate is said to be formed. I have not been able to verify this. I added a potassium hydroxide solution which, according to the literature, should produce a white precipitate with cerous salts that turns red on exposure to air, but I observed nothing of the kind.

14.5 Reactions with Organic Substances

Acetic Acid

- Pour water into a small beaker (no larger than 50 mL), preferably tall and narrow. Then slowly add acetic anhydride without shaking. It will be observed that the two liquids do not mix but produce a kind of shimmering movement at their interface.

Place the beaker on a hot plate and heat gently. The interface between the two liquids first becomes more sharply defined, after which bubbles or swirling currents appear between them. Little by little, exchanges occur between the two liquids. Strange interpenetrating patterns can then be observed. Once the entire liquid has become translucent instead of transparent, it suddenly becomes transparent again as the two components finally mix completely. The odor of acetic acid then becomes noticeable.
WARNING: To carry out this experiment, it is important to remain protected behind a transparent Plexiglas shield because this mixture is unstable and may suddenly be projected out of the beaker in all directions.

- In a flask fitted with a long tube surrounded by a wet cloth acting as a condenser, heat a moderately concentrated potassium permanganate solution containing a small amount of acetic acid. Pass the evolved gas into a wash bottle containing limewater or baryta water. The solution rapidly becomes cloudy, while water runs down the cooled tube.

- Pour 30 mL of lactic acid and 20 mL of concentrated sulfuric acid into a 100 mL flask. The mixture becomes dark yellow. Cover the flask with a stopper fitted with a duckbill delivery tube and heat gently. The liquid begins to foam while rapidly changing from dark yellow to brown and then black. Once the air has been expelled from the flask, ignite the gas issuing from the tube. It is carbon monoxide. The liquid soon becomes carbonized and gives off the odor of burnt sugar. For this reason, this mixture is of little practical use for the laboratory preparation of carbon monoxide.

- In a flask, prepare a 50:50 mixture of lactic acid and concentrated nitric acid. Then heat it. White fumes are evolved at first, followed by abundant reddish-brown nitrogen oxide fumes, which must not be inhaled. When the reaction is complete, slowly pour the liquid into a solution of a soluble calcium salt such as calcium chloride. A white precipitate, which sometimes appears only slowly, shows that oxalic acid has been formed.

- In a small flask, prepare a 50:50 mixture of pure lactic acid and a concentrated potassium permanganate solution. At room temperature, the mixture turns brown. Heat it. The liquid becomes completely clear, and acetaldehyde is evolved. It is readily recognized by its characteristic odor, which is somewhat reminiscent of apples.

Oxalic Acid

- Prepare a mixture of 15 mL of concentrated HCl and 15 mL of concentrated HNO_3 to produce aqua regia. Add a solution of 4 g of oxalic acid in 50 mL of water and bring it to a boil. Practically nothing particular is observed. Add a little manganese sulfate solution. Carbon dioxide is then evolved together with nitrous fumes, which must not be inhaled.

- When heated in an oxalic acid solution, indigo is decolorized very rapidly. Only a gray powder remains.

Picric Acid

PICRIC ACID = DANGER!

Picric acid is relatively uncommon in amateur laboratories in its solid form because of the hazards associated with its storage. In reality, safe storage is not difficult. Simply use a tightly sealed bottle. Place the moist solid picric acid in the bottom of the bottle and, inside it, place a smaller vial containing a piece of wet filter paper. Once the bottle has been sealed, the evaporation of the water will maintain the humidity required for safe storage.

- Place a small amount of picric acid, manganese dioxide, and two drops of H_2SO_4 in a small test tube (6 to 8 mm in diameter). Heat the mixture. Nitrous fumes are evolved. Only very small quantities should be used, and the reagents must be thoroughly mixed beforehand because picric acid explodes when heated alone.

- Dissolve picric acid in a small quantity of hot water, then allow the solution to cool slightly. Add excess ammonia until the solution becomes distinctly alkaline. Allow it to cool. Long red crystals of ammonium picrate appear. These crystals should be heated only with extreme caution, in very small quantities, and in aluminum boats because they detonate readily.

- Pour into an Erlenmeyer flask a mixture consisting of 1 part picric acid, 2 parts sodium cyanide, and 9 parts water. Bring the mixture to a boil. The liquid turns red. Allow it to cool. Crystals of sodium isopurpurate are deposited. A minute trace of ammonia may assist the reaction.

Tartaric Acid

- Place 2 or 3 cm of a tartaric acid solution and a small spoonful of manganese dioxide into a two-liter flask. Heat the flask and pass the evolved gas into limewater. The heavy calcium carbonate precipitate that forms and then disappears rather quickly shows that a large amount of carbon dioxide is being evolved. Continue heating for a short time, then allow the flask to cool. The characteristic odor of formic acid can then be detected.

- Mix a small quantity of tartaric acid with half its weight of resorcinol and immerse the mixture in concentrated H_2SO_4. Heat gently. A blood-red liquid is obtained. When diluted, this liquid becomes brown.

- Pour an aqueous potassium permanganate solution into an aqueous tartaric acid solution in an Erlenmeyer flask. A slight color change is observed. Close the flask with a stopper fitted with a tube leading to another flask containing baryta water. Heat gently. The baryta water becomes cloudy and white because of the evolution of carbon dioxide. Finally, the liquid in the Erlenmeyer flask begins to lose its color and soon becomes completely colorless.

Citric Acid

- Place an Erlenmeyer flask on a heated magnetic stirrer and bring a saturated solution of citric acid in ethyl alcohol to a boil. Add two drops of phenolphthalein to the clear solution. As soon as boiling is reached, stop heating and slowly introduce ammonia into the flask while stirring. At first, a white precipitate forms, but it gradually disappears until the liquid turns pink. Continue stirring until the cloudiness disappears. A slightly yellowish oily deposit of a form of ammonium citrate that does not crystallize is then observed at the bottom of the flask. Be sure to vent the flammable alcohol vapors outdoors.

Butyric Acid

- Pour a small quantity of butyric acid and an equal quantity of nitric acid into a narrow-necked 50 or 100 mL flask. The mixture should not fill more than half of the flask. Heat it without placing a stopper in the neck. At first, white fumes are evolved while the mixture boils vigorously and the liquid turns reddish-brown. Then, quite suddenly, the boiling appears to subside. Continue heating. Suddenly, a jet of liquid and gas is expelled from the flask. This jet may reach a height of more than one meter.
WARNING: this dangerous experiment must be carried out outdoors, and the operator should remain at least two meters away from the heat source. Standing behind a transparent protective screen is even better.

- Place one spatulaful of potassium permanganate, a small amount of water, and a little sodium hydroxide solution in a flask or Erlenmeyer flask. Finally, add an equal quantity of butyric acid and heat. Carbon dioxide is evolved, and the permanganate turns brown.

Tannin (Tannic or Gallotannic Acid)

- Mix concentrated H_2SO_4 with powdered tannin and stir. A yellow liquid is formed which, upon heating, turns brown and then purple.

- Add a small amount of manganese dioxide to a tannic acid solution and heat. Carbon dioxide evolution can be demonstrated by passing the gas into baryta water.

After the solution has cooled, a brown substance is found to have formed.

- When heated with a small amount of tannin, a potassium permanganate solution changes from violet to a dirty brown.

Sucrose and Glucose

- Place equal quantities of glucose and MnO_2 in a long test tube. Then pour concentrated sulfuric acid over the mixture and connect the test tube to a Drechsel bottle containing either baryta water or limewater. Gas evolution begins even at room temperature, but gentle heating greatly increases it and causes white fumes to fill the test tube. The carbon dioxide evolved rapidly turns the reagent cloudy. The odor of the fumes indicates that they consist of formic acid.

Figure 169

- Place 40 g of sugar and 200 mL of HNO_3 in a 2-liter flask. Heat gently. Reddish-brown nitrogen oxide fumes soon fill the flask and begin to escape. At this point, the heating may be stopped because the reaction continues by itself for a long time. Provide suitable venting for the fumes, as they are dangerous to inhale. Gradually, the reaction comes to an end. Heat the flask once more just enough to expel the last reddish-brown fumes, then pour the liquid into an evaporating dish and heat until its volume has been reduced by half. Finally, allow the liquid to evaporate slowly. Crystals of oxalic acid gradually separate from the solution (Figure 169).
WARNING: The experiment may also be carried out with various starchy materials or with pure starch. Work outdoors and remain well protected behind a safety screen, as this reaction may occasionally become explosive.

- In an old pharmacology book, I found the statement that an aqueous solution of glucose or sucrose, to which lead acetate and then a little aqueous ammonia had been added, produced a pink precipitate when heated. That is not at all what I observed! In fact, an aqueous lead acetate solution to which a little aqueous ammonia has been added already gives a white precipitate that turns pink upon heating and rapidly settles to the bottom of the test tube. Therefore, neither glucose nor sucrose is responsible for this coloration. In both cases, following the procedure described in the old book, I obtained a white precipitate in the cold. After boiling, no significant difference was observed. However, upon cooling, the test tube that had originally contained glucose produced a canary-yellow flocculent precipitate, whereas the precipitate in the sucrose test tube remained white.

Phenol

- Dissolve 30 g of phenol in 30 g of concentrated sulfuric acid with very gentle warming. Allow the mixture to cool. Transfer it to a very large flask (at least 2 to 3 liters) and add 100 g of concentrated HNO_3 diluted with an equal volume of water. The reaction is very vigorous, the temperature rises sharply, and abundant reddish-brown nitrogen oxide fumes are evolved. These fumes must not be inhaled. It is advisable to place the flask in a cooling bath. Once the reaction has subsided, heat the mixture gradually until the reddish-brown fumes are no longer produced. Cool the flask in an ice-water bath, then dilute the contents with ice-cold water. The solution becomes yellow, and crystals of picric acid precipitate. An oily substance remains in the flask and should be washed alternately with HNO_3 and water.
Another procedure, using different proportions, is as follows. Mix 1 part phenol with 5 parts H_2SO_4, then gradually introduce this mixture into 7 parts HNO_3 (specific gravity 1.38), stirring continuously while keeping the temperature below 10 °C (work in an ice bath). When the addition is complete, heat the mixture in a water bath at 80–90 °C until gas evolution begins. Allow it to cool. The liquid is then intensely yellow because of the picric acid that has formed.
The acid prepared in this way is not pure.
WARNING: Do not attempt to crystallize the picric acid, as its crystals then become markedly explosive.

- Pour a solution of phenol in chloroform into a flask or a Boro 3.3 glass test tube. Add a few grains of KOH and immerse the vessel in a water bath at approximately 80 °C. A somewhat vigorous reaction soon begins. The liquid changes from colorless to yellow, then to brown, and finally to pink (rosolic acid), while becoming increasingly viscous.
If carbon tetrachloride is used instead of chloroform and the vessel is immersed in a 100 °C water bath, the liquid first turns pink and then crystallizes completely.

- In a small flask, mix oxalic acid, phenol, and concentrated sulfuric acid. Heat gently. A pink coloration appears: it is rosolic acid. By continuing the heating and depending on the proportions of the reagents used, other dyes are obtained, such as yellowish-brown aurin or even corallin.

- Pour 3 or 4 mL of concentrated H_2SO_4 onto a pea-sized quantity of phenol and stir. At first, the liquid becomes slightly brown. Allow it to stand. Little by little, it changes to a delicate sky-blue color. If the liquid is stirred, a brownish-green zone appears where it comes into contact with the air. The entire liquid then becomes distinctly bluer. Heat the mixture. The liquid becomes lighter in color, then gradually turns very light brown before finally becoming charcoal black.

- Pour a small quantity of aqueous phenol into a test tube, then add mercury(II) nitrate. Heat the mixture. A red coloration appears.

- Fill a test tube to a height of about 5 cm with bleach, then carefully add enough

phenol to form a layer at the bottom. The phenol appears to dissolve slowly without any other visible change. Heat the test tube. The liquid turns brown, and a penetrating but rather pleasant odor is evolved. Trichlorophenol has been formed. However, it should not be inhaled in significant quantities because it is suspected of being carcinogenic.

- Place equal quantities of phenol and phthalic anhydride in a test tube (a ratio of 20 parts phenol to 15 parts phthalic anhydride may also be used), then add 3 or 4 drops of H_2SO_4. Heat until the liquid becomes red and then very dark, almost black. Allow it to cool, add water, stir to dissolve the mass, and filter through fine filter paper. It does not matter if the filtrate remains slightly black. Add the filtrate drop by drop to a solution of ammonia or sodium hydroxide. A red-violet color immediately appears because the filtrate contains phenolphthalein.
Some authors recommend prolonged heating in an oil bath at 150°C. It has seemed to me that this is entirely unnecessary if the objective is simply to demonstrate the reaction.

- The following experiment shows how to prepare a phenoplast-type resin. Begin by mixing 20 g of phenol with 25 g of 35% formaldehyde solution in a 200 mL beaker placed on a magnetic stirrer. Once all the phenol has dissolved, incorporate 55 mL of glacial acetic acid. A perfectly clear, very faintly colored solution is obtained. Remove the beaker from the stirrer and transfer 25 mL of its contents to a second 200 mL beaker, also placed on a magnetic stirrer. Then add 15 mL of 35% hydrochloric acid. At first, nothing appears to happen while the stir bar continues to rotate. Suddenly, after one or two minutes, the liquid abruptly becomes milky and then increasingly pink. Soon a solid mass forms, blocking the stir bar. Stop the stirrer, wait one or two minutes, and rinse the beaker. Inside is a rather dense pink sponge-like material in which the stir bar is trapped as though embedded in a matrix. The matrix is nevertheless easily broken apart to recover the stir bar. This pink material is a phenoplast resin which, once allowed to dry, remains perfectly stable (Figure 170).

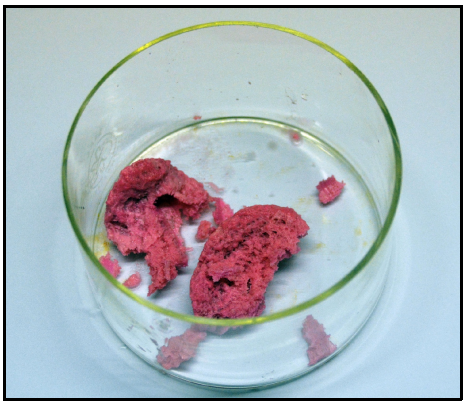


Figure 170

As described here, this experiment is completely safe. Nevertheless, the reaction may occasionally proceed rather abruptly. During the second stage of the experiment, it is therefore preferable to remain at a reasonable distance from the beaker.

Resorcinol

- Add sodium hypochlorite gradually to an aqueous resorcinol solution. The solution quickly turns violet to brown, then becomes yellow. On heating, this color may

disappear completely or turn brown, depending on the concentrations used (several trials may be necessary).

- Add dilute aqueous ammonia to an aqueous resorcinol solution. Nothing happens. Then, while stirring after each addition, add sodium hypochlorite drop by drop. A fleeting red color appears, and the solution becomes yellow. If it is then heated, it turns green to brown depending on the quantities used (several trials may be necessary).

- Prepare an aqueous solution of resorcinol and add a solution of sodium nitrite. Nothing happens at room temperature, but upon heating a yellow coloration appears.

- Place a small quantity of resorcinol in a test tube. Add 1 or 2 mL of potassium hydroxide solution. Even at room temperature, a faint yellow coloration appears after a few minutes. It becomes much more pronounced when heated to boiling. If a few drops of chloroform are added before heating, a pink to red coloration is obtained, depending on the relative concentrations of the reagents.

- Place a small amount of resorcinol in a large test tube and pour sodium hydroxide solution over it. A bluish-purple color appears. Add chloroform and shake. Two layers form, the upper one being pinkish-red while the lower one remains uncolored. Gentle heating changes the coloration to ruby red.

- Place a small amount of iodoform and two to three times as much resorcinol in a large test tube. Add 2 mL of ethyl alcohol and a few drops of sodium hydroxide solution. Boil the mixture for a short time. A red coloration is obtained.

- Mix 1 g of phthalic anhydride with 1.5 g of resorcinol in a small test tube, then add one or two drops of H_2SO_4. Heat gently until a red liquid is obtained. Immediately pour this liquid into a large quantity of water made alkaline with a little sodium hydroxide. The water at once develops a beautiful fluorescent yellowish-green color. Fluorescein has thus been prepared.
WARNING: This compound is capable of coloring enormous quantities of water. Avoid spilling it on the laboratory bench, as cleaning it up would take considerable time.

Formaldehyde (Formalin)

- Place approximately 1 cm of resorcinol powder in an ordinary test tube. Add 1 cm of water and 1 cm of formalin. Then add three drops of sodium hydroxide solution and heat gradually while stirring with a glass rod. The liquid changes progressively from pink to light brown. When it begins to boil, it thickens and soon can no longer be stirred. Break up the mass with the glass rod and transfer it to a crystallizing dish. Over the following days, this phenolic resin gradually darkens and hardens. The test

tube may be cleaned with aceton, provided this is done without delay.

- Place a small quantity of urea in a test tube and pour over it 3 cm of formalin containing one-fifth of its volume of hydrochloric acid. Even at room temperature, a white resin somewhat resembling Formica is produced. The reaction proceeds more rapidly with gentle heating.

- Pour a small quantity of Nessler's reagent (see its preparation in Chapter 3.2) into a test tube. Add a small quantity of formalin. The liquid becomes very dark gray. Heat and allow it to settle. A gray layer is deposited beneath a clear liquid. Pour off the liquid and add concentrated HNO_3. Reddish-brown nitrogen oxide fumes are evolved, and a beautiful brick-red precipitate forms, becoming even more distinct upon gentle heating.

Thymol and Menthol

- A solution of thymol in concentrated sulfuric acid gives a green liquid. Upon heating, it turns yellow, then gradually changes to orange, blood red, brown, and finally a dull pink. If the thymol is not pure or if the initial solution is no longer fresh, it tends to char.

- Dissolve a small amount of thymol in a potassium hydroxide solution, then add a few drops of chloroform and heat. A yellow coloration soon appears. It is sometimes necessary to add more chloroform to obtain a more intense coloration, which may, depending on the quantities used, change from orange to violet.
WARNING: Each time chloroform is added, be sure to extinguish the burner to eliminate any risk of explosion of the solvent vapors.

- Heat terpene hydrate in sulfuric acid diluted with fifty times its volume of water. A pleasant odor develops that has been compared with the fragrance of jasmine or hyacinth.
- Dissolve a small amount of thymol in acetic acid. Then add concentrated sulfuric acid and heat. A coloration ranging from yellow to purple is obtained, depending on the proportions of the reagents used.

- Place a small amount of thymol and one grain of KOH in a test tube. Pour 1 mL of chloroform over the mixture and heat gently. The color soon changes from pink to reddish-violet.

Urea

- Cover the bottom of a large flat-bottomed flask with urea and pour concentrated H_2SO_4 over it. Close the flask with a rubber stopper fitted with a T-tube. One branch of the T-tube is closed with a small rubber stopper, while the other leads to two

wash bottles connected in series. Place a piece of moistened indicator paper in the first wash bottle and a small amount of baryta water in the second. Heat gently. The indicator paper shows a strongly alkaline pH because ammonia is evolved. The baryta water becomes cloudy because carbon dioxide is also evolved.
If hydrochloric acid had been used instead of sulfuric acid, the indicator paper would first have shown an acidic pH because of the initial evolution of hydrogen chloride, then it would have turned alkaline as ammonia was evolved, while a cloud of ammonium chloride formed in the wash bottle.
If the acid is replaced with sodium hypochlorite, carbon dioxide and nitrogen are evolved, although the latter is not easily identified. Gas evolution begins even at room temperature and continues during heating.
WARNING: This reaction may occasionally accelerate unexpectedly and produce a large volume of gas. For this reason, a flask should be used rather than an Erlenmeyer flask, and its volume should be four to five times greater than the initial volume of the reagents. If the reaction accelerates, gas dispersion can be facilitated by removing the small stopper closing the second branch of the T-tube fitted into the rubber stopper. The gases evolved are neither toxic, nor oxidizing, nor explosive.

- Prepare a concentrated aqueous urea solution and divide it into three portions. Heat the first portion. The evolution of NH_3 and CO_2 is observed. Add a little sodium hydroxide solution to the second portion and heat. This time, only NH_3 is evolved. Add dilute sulfuric acid to the third portion and heat. This time, only CO_2 is evolved.

Naphthalene

- Place naphthalene in concentrated nitric acid and heat. The naphthalene rapidly disappears while the liquid turns yellow and reddish-brown nitrous fumes appear. Stop heating and allow the mixture to cool. Yellow crystals of nitrated naphthalene are obtained. They dissolve in water to give a yellowish-white liquid. By continuing the boiling or by adding H_2SO_4, other derivatives (dinitronaphthalene, trinitronaphthalene, tetranitronaphthalene, etc.) would be obtained. These compounds become progressively less soluble in solvents and melt at increasingly higher temperatures.

- Dissolve naphthalene in acetic acid, add approximately an equal volume of nitric acid, and heat under reflux for half an hour. At the very beginning, the liquid rapidly turns yellow while a burst of reddish-brown nitrogen oxide fumes is evolved. The fumes then cease, and the color of the liquid no longer changes. Allow it to cool, then add water, stir, and let the mixture stand. At first, the liquid becomes completely cloudy and takes on a sulfur-yellow color. Then, over the course of about half an hour, an insoluble yellow globule settles to the bottom, while very fine water-soluble crystalline needles emerge both from the bottom and from the surface of the liquid (Figure 171).

Figure 171

- Place 8 parts of naphthalene and 3 parts of concentrated H_2SO_4 in a Kjeldahl flask of at least 500 mL capacity, held vertically. The mixture should fill no more than one quarter of the bulb of the flask, and preferably even less. Heat gently. The naphthalene gradually disappears in the acid and, at a little above 180°C, a black carbonaceous material falls to the bottom of the flask while white fumes are evolved and crackling sounds are heard. Allow the flask to cool after covering its neck with a watch glass. The entire flask soon becomes filled with feather-like crystals that initially float in the liquid before gradually adhering to the inner walls of the flask. Then pour in 4 parts of boiling water. Two different substances can now be observed: one brown and the other greenish. The flask can afterwards be cleaned easily with aceton.

Camphor

- Heat camphor in dilute nitric acid. A thin film first forms on the surface of the liquid, after which the characteristic odor of camphoric acid becomes noticeable. Camphor tends to sublime rather quickly. Consequently, the ideal arrangement appears to be heating under reflux with a vertical condenser open at its upper end, allowing both the acid vapors and the camphor to condense continuously and flow back into the flask.

- Place camphor and sulfuric acid in a test tube. Even at room temperature, the acid begins to turn yellow. Upon heating, the liquid becomes red and finally completely black.

Aniline

- Place approximately half a cubic centimeter of powdered benzoic acid, together with a lancet-tip quantity of fuchsin, into a 100 mL flask or Erlenmeyer flask. Cover the mixture with aniline and heat gently, either over a low flame or in a boiling-water bath, for about ten minutes. The oily liquid appears ruby red when viewed by transmitted light. However, it is sufficient to pour a few drops into water or, even better, into ethyl or methyl alcohol to obtain the characteristic purple color commonly known as aniline blue. When poured into water, the liquid mixes only with difficulty. If ammonia is added, it turns yellow. If a few drops of H_2SO_4 are added instead, it becomes green. he flask is easily cleaned with alcohol.

- Place 1 cm of aniline and 1 cm of HNO_3 in a large test tube. Heat gently. A blue or green coloration appears.
WARNING: The reaction tends to accelerate unexpectedly, producing reddish-brown nitrogen oxide fumes and extensive charring.

- Sulfur dissolves very readily in boiling aniline, forming a variety of complex products. If the solution is cooled rapidly, it may solidify completely before partially

liquefying again.

- Dilute sodium hydroxide in approximately 60 mL of ethyl alcohol and divide the solution into two portions, each placed in a small 100 mL flask. Pour a small amount of chloroform into each flask, then add two or three drops of aniline to one of them. Heat both flasks (without an open flame, because of the explosive vapors of chloroform). In the flask containing no aniline, a white cloud of sodium formate rapidly forms. In the second flask, a precipitate appears together with a persistent, highly unpleasant-smelling substance known as phenyl carbylamine, or phenyl isocyanide (C_6H_5NC).

- Pour 1 to 2 mL of chloroform into a test tube, followed by 1 to 2 mL of a freshly prepared alcoholic potassium hydroxide solution, and finally 2 or 3 drops of aniline. Heat the mixture. The liquid becomes white and lumpy while the unpleasant odor of toxic isocyanobenzene appears. Avoid inhaling this substance.

- Place a lancet-tip quantity of PbO_2 in a test tube, then add a few drops of concentrated nitric acid. Finally, add one or two drops of aniline. A green coloration is obtained which, upon heating, changes first to blue and then to red.

- Pour 0.5 mL of concentrated nitric acid into a test tube, then add a lancet-tip quantity of potassium dichromate. Stir, then add one drop of aniline. Upon stirring, several colors appear, including yellow, blue, and green. Upon heating, the liquid becomes red.
WARNING: When heated, a flame may occasionally erupt suddenly from the test tube. For this reason, only very small quantities of reagents should be used.

- Pour 0.5 mL of concentrated nitric acid into a test tube and add a lancet-tip quantity of potassium permanganate. Stir, then add one drop of aniline. A coloration is obtained that may vary from red to blue through green, especially if the mixture is heated gently.

- Pour 50 mL of water into a 250 mL flask, then add 1 mL of aniline. The aniline forms insoluble droplets. Add 20 mL of acetic acid. The aniline then dissolves to give a very pale yellow solution. Heat the mixture very gently and add a small amount of sodium nitrite solution. The liquid immediately takes on a golden-yellow color, but this is only temporary. As the solution warms, opaque clouds appear, successively passing through orange, brick red, burnt sienna, then finally brown and black. If less nitrite is added, the solution remains a very dark yellow. Add a little hydrochloric acid and stir. A very dark red liquid is now obtained, although it remains transparent when viewed in a thin layer. If sodium hydroxide is then added, the solution turns yellow. A genuine acid-base indicator has thus been prepared.
As is often the case with aniline derivatives, the flask may afterwards require cleaning with aceton.

- Mix a few particles of iodoform with 1 or 2 mL of aniline and boil the mixture

briefly. A red coloration is obtained. If too much iodoform has been used and the color is excessively intense, simply dilute it with alcohol.

- Pour a few drops of concentrated nitric acid into a test tube, then add a lancet-tip quantity of manganese dioxide. Stir and add one drop of aniline. Upon heating, the very dark liquid gradually turns reddish-brown.

Miscellaneous

- Sodium formate has the property of extracting the metal from certain salts when they are present in a mixture of two salts. For example, it can extract mercury from a solution containing both a mercury salt and a copper salt. This may be demonstrated in three stages.
Prepare a sodium formate solution and add a small quantity of it to a mercury nitrate solution. Do the same with a silver nitrate solution. Heat both mixtures to boiling. In each case, the color changes and the metal (mercury or silver) precipitates.
Next, prepare a mixture of copper nitrate and mercury nitrate solutions. Add an aqueous sodium formate solution and bring the mixture to a boil. Again, the color changes and, upon cooling, mercury is deposited.

- Prepare a small quantity of Fehling's solution, having its characteristic sky-blue color, in a test tube. Add a few drops of chloroform and heat cautiously. The color gradually changes from green to brown. Allow the mixture to settle. A layer of red cuprous oxide is then deposited.

- Heat a small quantity of amyl alcohol with potassium dichromate and a little H_2SO_4 in a small flask. The liquid rapidly turns green and then bluish-green, while a pleasant odor escapes from the flask. It consists of a mixture of aldehyde and, above all, valeric acid.

- Heat a small quantity of amyl alcohol with sulfuric acid and acetic acid in a small flask. The liquid soon becomes pink, then red, and finally brown, while a pleasant pear-like odor, due to amyl acetate, escapes from the flask.
WARNING: Amyl acetate is flammable. Therefore, extinguish the Bunsen burner as soon as its odor becomes noticeable or, preferably, use electric heating.

- If iodoform is heated with nitric acid or sulfuric acid, iodine is rapidly liberated in both cases. The final color of the liquid, however, differs greatly depending on which acid is used.

- Place a lancet-tip quantity of salicylic acid in a test tube. Add 2 cm of water and warm gently to facilitate dissolution. Then add a copper sulfate solution. The color changes to ink blue. Bring the mixture to a boil. The color then changes to duck blue

- Dissolve a small amount of acetylsalicylic acid (formerly sold exclusively under the trade name Aspirin) in water in a small Erlenmeyer flask, then add a little sodium hydroxide. Bring the mixture to a boil and allow it to cool. If concentrated H_2SO_4 is then added, either turbidity or a precipitate is produced, depending on the concentrations used.

- Identifying the presence of ethanol by means of a dilute aqueous potassium permanganate solution that changes color is a fairly classical analytical method. There is, however, another way to react potassium permanganate with ethyl alcohol. Place a flask containing ethyl alcohol on a heated magnetic stirrer. Begin by adding a quantity of potassium permanganate approximately the size of a quarter of a pea and start the stirrer. The liquid soon turns violet, but nothing else happens. Add another spatulaful of potassium permanganate and fit the flask with a straight water-cooled condenser. Heat gradually. The liquid rather quickly assumes a wine-red color and then changes to light or dark brown, depending on whether more potassium permanganate is added through the top of the condenser. The alcohol begins to boil. Allow the reaction to continue for a few minutes before switching off both the heating and the stirring. Remove the still-warm flask from the stirrer and allow the contents to cool before decanting them into a tall test tube. A brown substance is then seen to settle. Separate it from the liquid and bring it into contact with hydrochloric acid. Chlorine is evolved, thus identifying the substance as manganese dioxide.

- In a large test tube (approximately 25 to 30 mm in diameter), mix a knife-tip quantity of terpin hydrate with 3 cm of water and heat. A clear solution is rapidly obtained. Add 1 to 2 cm^3 of sulfuric acid diluted 1:1 with water and heat again. The solution becomes cloudy and gives off a pleasant aromatic odor. Terpineol has been formed, a compound widely used in perfumery. Hydrochloric acid may be used instead of sulfuric acid, although the result is less satisfactory.

- Place a small amount of terpin hydrate in a test tube and add two or three drops of H_2SO_4. Even at room temperature, the substance begins to turn pink. Upon heating, it develops a beautiful red color.

- Add a small amount of sodium hydroxide solution to water containing starch, then add iodine solution. A purple or nearly black liquid is obtained, depending on the amount of iodine solution used. Gradually, however, the liquid loses its color, becoming reddish and then pink. Heating accelerates the reaction, and at the boiling point the liquid becomes completely clear after first taking on a milky appearance.

- Pour 200 mL of water, 10 mL of concentrated sulfuric acid, and one small teaspoonful of rice or wheat starch into a tall vessel. Mix thoroughly and introduce steam through a wide tube connected directly to a flask of boiling water. Stir the mixture continuously. Little by little, the liquid becomes clearer. Periodically test small samples with iodine solution. At first, a blue-black coloration indicates the presence of starch. After some time, this changes to reddish-brown because the

starch has been converted into dextrin. Finally, after at least twenty minutes, iodine solution no longer produces any coloration because glucose has been formed. Pour the hot liquid into a large beaker and neutralize the remaining acid with powdered potassium carbonate. Vigorous foaming occurs, accompanied by the evolution of CO_2 and the precipitation of insoluble calcium sulfate. If the mixture becomes excessively pasty and continues to react after further additions of potassium carbonate, a little water may be added. When additional carbonate no longer produces any reaction and the pH has become neutral, filter the mixture through a Büchner funnel, since an ordinary funnel would operate too slowly because of the highly pasty consistency of the mixture. An almost colorless liquid is obtained. Evaporate it in an evaporating dish until it reaches a more syrupy consistency. Upon cooling or by allowing it to evaporate slowly in air, the solution finally crystallizes. The glucose obtained may be tasted and may also be used in a Fehling's solution test.
Many people would be surprised to learn that, in the past, some small trays of gelatinous jam sold commercially were made from glucose obtained by treating old cotton rags with sulfuric acid. The glucose produced in this way formed the principal ingredient of these widely appreciated delicacies.

- Place 15 g of aceton and 30 g of concentrated but not fuming nitric acid in a 250 to 300 mL flask. A white cloud immediately appears. Heat gently outdoors in a well-ventilated open area. The white cloud gradually disappears, and the first bubbles appear in the liquid. Stop heating immediately and move at least 2 meters away from the apparatus. After a short time, the reaction suddenly accelerates violently. Liquid is projected from the flask while torrents of reddish-brown NO_2 fumes are evolved (Figure 172).
WARNING: Because this reaction also produces hydrogen cyanide, this dangerous experiment must be carried out outdoors in a well-ventilated open area.

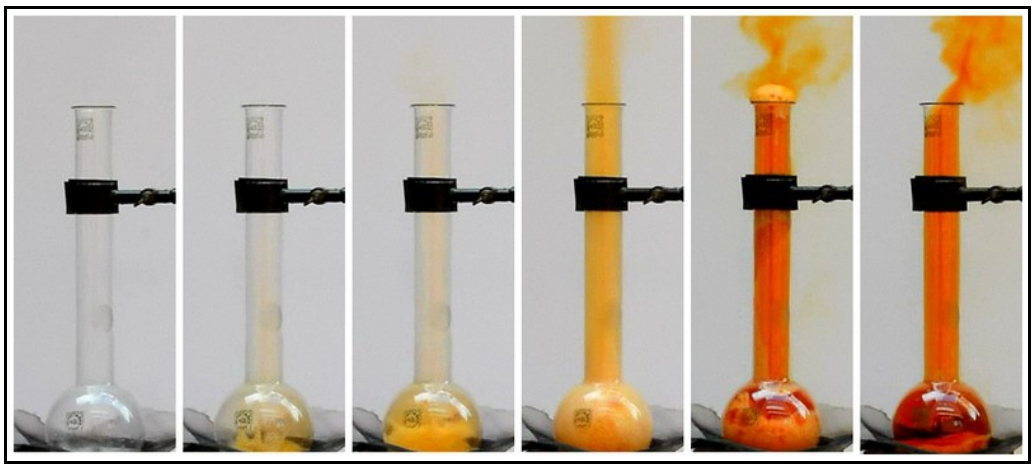


Figure 172

- Pour a small quantity of ethyl acetate into a large test tube and immerse a pH indicator strip. It will be found that the liquid is not acidic. Add an equal volume of water, mix, and heat. The liquid becomes acidic because acetic acid has formed. The same change occurs if the mixture is stirred for a prolonged period without heating.

- Prepare, while heating, a solution of 6 g of borax and 5 g of boric acid in 100 mL of water. Soak a cotton cosmetic pad or a ball of absorbent cotton in the solution, squeeze out the excess liquid, and allow it to dry. When completely dry, ignite the cotton with a match or a small torch. It does burn, but only slowly and without a flame. It has been rendered flame-resistant. This was formerly the method used to prevent cotton clothing from catching fire and causing severe burns.

- Place one teaspoonful of gum arabic in an Erlenmeyer flask and cover it generously with well-diluted sulfuric acid. Heat until the liquid boils and becomes clear and brown, no longer producing foam. Allow it to cool and smell the odor released from the flask. It is the familiar smell of homemade caramel. Test the solution with Fehling's solution. A red precipitate is obtained, indicating the formation of glucose.

- Place two teaspoonfuls of sawdust in an Erlenmeyer flask of at least 300 mL capacity and cover it with concentrated H_2SO_4. Heat and pass the evolved gases first through a Drechsel bottle containing baryta water and then through a second Drechsel bottle containing either an aqueous potassium permanganate solution or even red wine. The evolution of CO_2 and SO_2 is readily demonstrated: a white precipitate forms in the first Drechsel bottle, while the potassium permanganate solution—or the red wine—is decolorized in the second.

- Few people realize that they perform chemistry simply by cooking an egg. Heat coagulates egg albumin, but albumin may also be coagulated at room temperature by acids, alcohol, or ether. All of these experiments are easily carried out in a simple test tube.

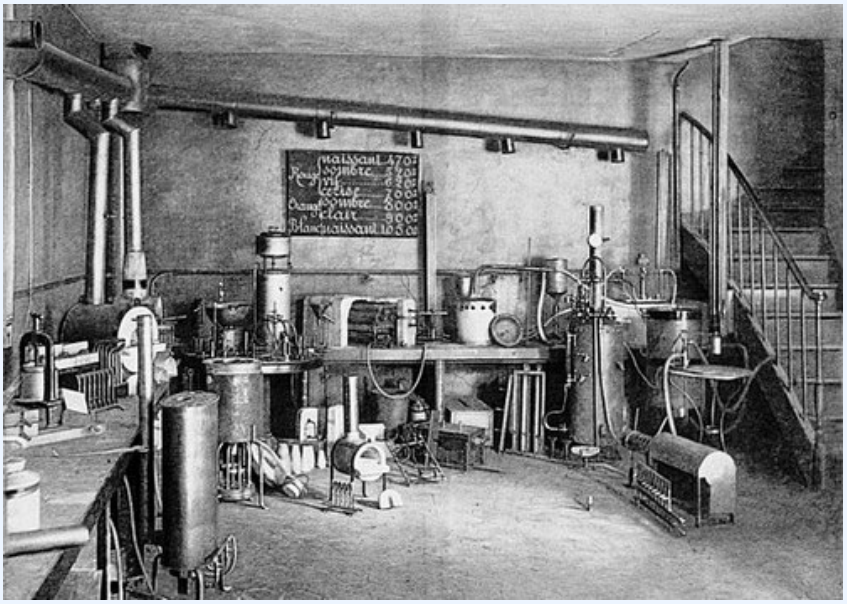
- Pour nitric acid onto egg white and heat. A yellow coloration is obtained, identical to that produced on the skin by a burn with nitric acid. If ammonium hydroxide is then added, the color changes to orange.

- Egg white is by far the best-known source of albumin. It is worth remembering, however, that albumin also occurs in many other biological materials. One example is semen, which may likewise be made to react with heat, acids, alcohol, and ether, giving results similar to those obtained with egg albumin.

- Unlike albumin, gelatin is soluble in hot water, although it is likewise precipitated by alcohol and ether.

WHAT DID CHEMISTRY LABORATORIES LOOK LIKE AT THE END OF THE 19TH CENTURY?

(From the atlas accompanying Edmond Frémy et al.'s Encyclopédie chimique, Paris: Dunod, 1882.)



Chapter 15 - Distillations and Other Similar Operations

15.1 Extractions

In certain cases, mainly involving organic chemistry, it may be necessary to extract a substance from a solid material, such as plants, by using a suitable solvent. A special apparatus known as a Soxhlet extractor, named after its inventor Franz von Soxhlet (1848–1926), is then employed. This apparatus resembles a cylinder fitted with two side tubes, one fairly wide and the other narrow, bent back on itself to form an inverted U-shape.

Figure 173

The Soxhlet extractor is always surmounted by a condenser. Professionals generally choose a Dimroth condenser, named after its inventor Otto Dimroth (1872–1940), in which cold water circulates through a central single or double coil. It is therefore on this coil that the vapors condense. Although this type of condenser is highly efficient, it is also much more fragile and expensive than a conventional condenser and is by no means indispensable.

To extract, for example, the coloring principle of logwood using ethyl alcohol, pieces of logwood are first placed in the central chamber of the Soxhlet extractor, taking care to plug its small side tube with a cosmetic cotton pad, which makes it possible to dispense with the expensive special thimbles normally intended for use in this apparatus. The pieces of logwood could just as well be enclosed in a fine curtain fabric. The purpose of the cotton pad or fabric is simply to prevent small fragments of material from becoming lodged in the narrow side tube of the Soxhlet extractor, from which they would later be impossible or very difficult to remove (Figure 173).

The alcohol is placed in a ground-neck flask to which the Soxhlet extractor is attached, and the condenser is mounted above it. The flask is then heated. Alcohol vapors rise through the wide side tube of the Soxhlet extractor and enter the condenser, where they are condensed and fall back as a warm liquid into the central chamber of the extractor. There, the liquid bathes the pieces of logwood until its level reaches the bend of the narrow side tube. A siphoning action then begins, and all the liquid contained in the Soxhlet extractor returns to the main flask, where it is heated once again. Thus ends a first extraction cycle, followed by as many others as necessary until the liquid bathing the fragments of logwood runs off almost colorless. At that point, the extraction of the coloring principle may be considered complete.

Another example : A Soxhlet extractor is filled with carrot reduced to very small pieces after placing a carrot in a blender or coffee grinder. The Soxhlet is attached to a flask containing a mixture of cyclohexane (80%) and ethyl alcohol (20%) in an amount proportional to the volume of the Soxhlet. Heating is carried out with an electric heating mantle (avoid the flame of a Bunsen burner!) after fitting the Soxhlet with a suitable condenser. From the outset, care has been taken to plug the outlet of the Soxhlet with a cotton plug. Nevertheless, a certain quantity of very fine material will pass through this plug, so that at the end of the operation the contents of the flask must be filtered. Two layers will then be seen: the upper solvent layer and the lower layer consisting of cloudy water originating from the carrot itself. The solvent contains the bright yellow beta-carotene. Attention: this substance is sensitive to heat and light. If one wishes to evaporate the solvent, it is therefore better to work in darkness. Other solvents may of course be used, but this mixture appears to be the most effective (Figure 174).

Figure 174

15.2 Distillations and Reflux Heating

Distillation apparatus is used in three different situations:
1)To liquefy a substance that is released from a reaction in the form of vapors.
2) To concentrate a liquid substance.
3) To separate a substance from a mixture whose components have markedly different boiling points.

In the first case, the apparatus merely serves as a cooling device. In the second, a simple distillation is carried out. In the third, a so-called fractional distillation is performed with the aid of a Vigreux column or a Raschig-ring column.

Depending on the circumstances, the apparatus may consist simply of a distillation flask with a side arm and a condenser assembled with rubber stoppers, or of much more complex glassware allowing the periodic addition of a reagent, the collection of a liquid protected from air while permitting the escape of certain gases, or even operation under reduced pressure, which makes it possible to lower the distillation temperature.

Reflux heating, on the other hand, consists in a sense of continuously distilling the same substance in a closed circuit. To do this, a condenser is placed directly above a flask or, better still, above a column mounted on the flask. In this way, vapors condensed first in the column and then in the condenser continuously return to the flask. The type of condenser is chosen according to whether the vapors require strong cooling or not.

Here is a typical experiment in which the condenser is used to collect, in liquid form, a substance initially produced as a vapor. A given weight of thoroughly dried sodium acetate is placed in a two-neck ground-glass flask. Through a stopcock funnel fitted to one neck of the flask, an equal weight of concentrated sulfuric acid is allowed to flow into the flask. The reaction already begins in the cold, but gentle heating is then required so that vapors are evolved. These pass through the second neck into a condenser and are subsequently condensed in a receiving flask. The odor alone clearly reveals that acetic acid is being distilled.
NOTE: For reasons of economy, in a school for example, and provided that the purpose is not to demonstrate the mechanism of distillation itself, one may of course simply heat a test tube containing the same mixture. The odor alone is sufficient to make the reaction understandable.

A VERY USEFUL ADAPTER...

When carrying out distillations, I recommend always connecting the condenser to the receiving flask by means of the special adapter normally used for vacuum or reduced-pressure distillations (see illustration).

Equipped with a side-arm fitted with a hose connection, it makes it easy to vent any toxic or explosive vapors outdoors through a flexible tube. Many risks of explosion or poisoning can thus be eliminated.

15.3 Mixtures with Alcohols

15.3.1 Perfumed Esters

Among the "classics" of experimental organic chemistry are the preparations intended to produce particular esters whose odors are reminiscent of certain fruits, rum, or vanilla. These reactions are in fact the basis of the industrial production of certain synthetic flavorings and perfumes used, for example, in the food industry. However, there is a vast difference between what can be achieved industrially by precisely controlling a whole series of parameters or successive operations and what can be obtained in a small laboratory. In the latter case, it is important to point out that a certain amount of imagination is always necessary in order to recognize, by smell alone, a perfumed ester. And, why not say it openly: sometimes the odor that remains in the laboratory afterward can be particularly unpleasant...

- While cooling thoroughly and pouring the acid into the alcohol rather than the reverse, prepare a mixture of one part methyl alcohol and one part concentrated sulfuric acid. This mixture is then poured into two parts of butyric acid already contained in a 500 mL flask. The whole is then distilled. The liquid that distills is a mixture containing methyl butyrate, whose odor is supposed to resemble that of a greengage plum.
If methyl alcohol is replaced by ethyl alcohol, ethyl butyrate is obtained, which is supposed to have the odor of rum.
To obtain these esters in a pure state, they should be shaken with salt water and then dried over calcium chloride, a procedure that is rarely carried out in a small laboratory because of the small quantities obtained.
WARNING: As already mentioned, the odor of butyric acid is undoubtedly one of the worst that can invade a chemistry laboratory. It is a strong smell of rancid butter, but also of mice or liquid manure. Care should therefore be taken never to spill even a small amount of this acid onto an inconspicuous porous surface, since the laboratory could become uninhabitable for days or even weeks if the exact location requiring neutralization cannot be identified. In such a case, the only possible remedy is to heat a concentrated ammonia solution periodically in an evaporating dish and then ventilate the entire room thoroughly.

- Gaseous hydrogen chloride is bubbled through a mixture consisting of equal parts formic acid and ethyl alcohol. The mixture is left to stand overnight and is then distilled. The distillate has a strong odor that may recall a mixture of rum and raspberry; it is ethyl formate, formerly used to dissolve photographic films and to flavor certain pastries.
A second method for obtaining this substance is as follows: place 35 g of thoroughly dried sodium formate in a flask, then add a cold mixture of 50 g of H_2SO_4 and 30 g of 90–94% ethyl alcohol. Heat very gently. White vapors appear and the formate rapidly distills.

There is a third way to proceed: place in a flask a mixture of 100 mL of H_2SO_4 and 100 mL of ethyl alcohol prepared by pouring the acid into the alcohol while cooling vigorously. Then add 75 mL of formic acid and distill.
In all three cases, violent bumping may occur in the liquid being distilled. Fragments of pumice stone or fired clay (broken flowerpot) should therefore be added. The flask should also preferably be fitted with a Vigreux column or a Raschig-ring column. Ethyl formate then distills first and is collected until the temperature, which has remained constant up to that point, rises toward a second plateau.
Colorless ethyl formate boils at 53.4°C and burns with a colorless flame edged with red. Since the vapors of the distillate are highly flammable, it is imperative to ensure that the apparatus is perfectly leak-tight.
NOTE: A "cold" method for preparing ethyl formate is possible because of its low boiling point. It is sufficient to place the sodium formate and alcohol in the flask and then add the acid. Heating immediately occurs without the need for any external source of heat, and the ester distills at once.

- Prepare a mixture of acetic acid and amyl alcohol (equal parts) and add a little H_2SO_4. Distill the mixture. Since the reaction is rather vigorous, it is preferable to place a few fragments of pumice stone or fired clay in the flask. The liquid changes from clear to red and then becomes very dark. A synthetic essence having the odor of pear distills over.

15.3.2 Other Esters

- While cooling thoroughly, mix 5 parts of ethyl alcohol with 9 parts of H_2SO_4 (for example, 150 mL of alcohol with 270 mL of H_2SO_4). Place this mixture in a three-neck flask or in a single-neck flask fitted with a triple adapter. Through the central neck or the central branch of the adapter, insert a thermometer reaching down into the liquid. On another neck or branch of the adapter, place a stopcock funnel containing ethyl alcohol. The third neck or branch of the adapter leads to a condenser fitted at its end with a bent adapter provided with an air inlet (see the boxed note of page 441) and a small receiving flask. Heat the apparatus. The mixture begins to turn yellow and then brown. Various vapors are evolved from 120°C onward. When the temperature of the liquid rises above 140°C, add alcohol, which is progressively consumed while the quantity of H_2SO_4 remains constant. At the outlet of the condenser, a mixture of ether and alcohol is collected. This mixture forms two layers that can easily be separated by means of a separatory funnel.
WARNING: Ether vapors are highly explosive. It is therefore essential to ensure that they cannot come into contact with a flame, but also with the intense heat that may be generated, for example, by an electric hotplate. The best precaution is therefore to ensure scrupulously that the apparatus is perfectly leak-tight and that unrecovered vapors and gases are discharged directly outdoors.

- In a one-liter two-neck flask, mix 39 g of MnO_2, 39 g of concentrated H_2SO_4, and 26 g of water. Fit one neck with a stopcock funnel containing 26 g of absolute ethyl

alcohol. The other neck supports an adapter leading on the one hand to a condenser and on the other hand allowing measurement of the temperature at the entrance to the condenser. Add a little alcohol to the flask and heat gently. Boiling begins, its intensity being moderated by fragments of pumice stone. Continue heating moderately while gradually adding the remainder of the alcohol. During distillation, (impure) acetal passes over and can be recognized by its pleasant odor.

- Place 50 g of powdered potassium nitrate in a distillation flask and pour over it a mixture of 100 g of sulfuric acid and 50 g of methyl alcohol that has previously been prepared with continuous cooling. Connect the flask to a condenser and the condenser to a receiving flask immersed in an ice-water bath. Heat slowly. Methyl nitrate distills over. It has a pleasantly ethereal odor, and a few drops placed in an evaporating dish can easily be ignited with a match. The flame is hot and slightly bluish. Care should be taken to ensure the leak-tightness of the apparatus because of the flammability of the distillate.

- In a flask, mix equal quantities of amyl alcohol and concentrated HCl, ensuring that the total volume of liquid does not exceed one-third of the volume of the flask. Heat gradually, since boiling is vigorous (it may therefore be useful to add a few fragments of pumice stone or fired clay). The liquid becomes golden yellow, after which invisible vapors begin to distill and condense into a slightly syrupy yellowish liquid composed of HCl and amyl chloride (chloropentane), whose characteristic and suffocating odor is unmistakable. This product emits dense white fumes when brought into contact with water.

- While cooling thoroughly, mix 100 g of H_2SO_4 with 100 g of methyl alcohol (pouring the acid into the alcohol and not the reverse) and place the whole in a 500 mL flask previously charged with 100 g of oxalic acid. Distill in the usual manner while collecting the distillate in a flask surrounded by ice. Two different compounds are obtained: a colorless liquid that burns with a barely visible but hot flame, and a solid consisting of small white flakes, namely methyl oxalate. Mixed with ammonia, the liquid gradually produces a white precipitate of oxamide.

- Place 60 g of sodium bromide in a 250 mL two-neck flask. Fit the side neck with a stopcock funnel containing a mixture of 25 g of ethyl alcohol and 50 g of H_2SO_4, prepared beforehand by pouring the acid into the alcohol while cooling vigorously. The vertical neck is fitted with a Vigreux column connected to a conventional straight condenser leading, through an adapter such as that described in the boxed note on page 441, to a receiving flask containing a little water and placed in an ice-water mixture. Begin the operation by allowing the entire contents of the funnel to run into the flask before starting to heat. The contents of the flask become orange and foam, but in a reasonable manner. Ethyl bromide is finally evolved and collected. This highly volatile ethyl bromide (its boiling point is only 38°C) collects beneath the layer of cold water.

- Citric acid is dissolved in methyl alcohol in a water bath at 60°C. The solution is

then cooled and gaseous HCl is bubbled through it. Finally, the mixture is distilled through a Vigreux column in order to collect methyl citrate. Sometimes the latter is already visible in the liquid from the outset because of its different refractive properties.

- Place an amount of salicylic acid the size of a pea in a test tube. Pour 2 mL of methanol over it, followed by 2 mL of concentrated sulfuric acid. Heat gently. The vapors that are released have a very pleasant odor. They consist of an ester, methyl salicylate, known as oil of Wintergreen. Although currently very fashionable as a pain-relieving remedy on certain social networks and websites devoted to alternative medicine, it should nevertheless be treated with great caution outside strict medical supervision. The experiment described here should therefore be regarded only as a laboratory curiosity.

- The preparation of ethanal (acetaldehyde) is complicated, and most authors provide highly contradictory information on the subject. One states that the operation must be carried out in the cold, another at 60°C, a third at 80°C, and a fourth at 100°C. I shall not even discuss the quantities of reagents to be used, whose proportions vary considerably from one author to another, nor the apparatus to be employed, which is described in very different ways here and there. Since the present work is not intended for university laboratories, here is the rather simple method that I recommend...
A 2-liter flask with an elongated ground-glass neck is taken and charged with 30 g of potassium dichromate, over which 60 mL of distilled water are poured. This flask has two necks, or alternatively one neck fitted with an adapter allowing two pieces of apparatus to be attached. The first is a stopcock funnel containing a mixture prepared as follows: 40 g of sulfuric acid are poured onto 30 g of ethyl alcohol while cooling vigorously, after which 60 mL of water are added, again while cooling. The second piece of apparatus is a vertical condenser that will serve as a reflux condenser.
A glass tube leaves the top of this condenser and is connected to a U-tube containing 100 mL of ether and immersed in an ice-water bath. The outlet of the U-tube is connected to the ventilation system. When the U-tube containing the ether has been thoroughly cooled, the flask is heated and a few drops of the mixture contained in the stopcock funnel are allowed to fall into it. When it is observed that these drops produce vigorous boiling, heating is discontinued and the flask continues to be supplied dropwise with the liquid contained in the funnel.
The reaction releases a great deal of heat and may foam strongly, hence the need for a large flask. The reflux condenser causes droplets to return continuously to the flask. The movements of the ether in the U-tube reveal that a gas is being evolved. When the funnel has been completely emptied, the flask is heated again gently for a short time.
The second part of the operation can then begin. The U-tube is connected to a flask in which ammonia is heated with a little charcoal. Ammonia gas is evolved and, before reaching the U-tube, first passes through a tube filled with pieces of quicklime in order to dry it. A white precipitate is then observed to form in the

U-tube. This precipitate must be collected and washed with ether.
Only then is the third part of the operation carried out: the ammoniacal compound is mixed with dilute sulfuric acid and then distilled. Ethanal is thus finally obtained as a very mobile, colorless liquid having a suffocating odor.

- While cooling thoroughly, prepare a mixture of 6 mL of H_2SO_4 and 15 mL of methyl alcohol (pouring the acid into the alcohol and not the reverse). Next, cover the bottom of a 150 mL Erlenmeyer flask with crystals of boric acid. Then pour the alcohol/acid mixture into the Erlenmeyer flask and close it with a stopper pierced by a tube bent at 90° and ending in a duckbill outlet. Place the flask on wire gauze supported by a tripod and heat gently. The alcohol begins to boil. Wait four to five seconds and, when a "vapor" is seen emerging from the end of the bent tube, bring a match to it. A large green flame is obtained: that of burning methyl borate.

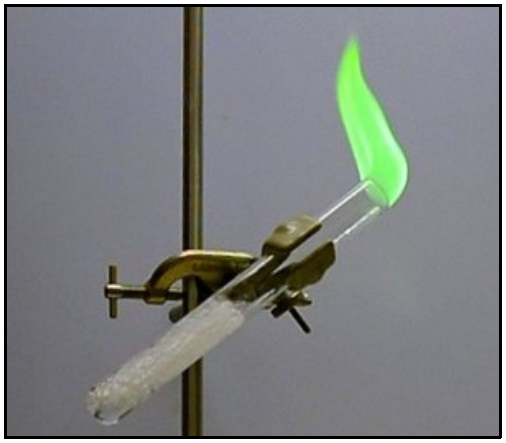


Figure 175

This experiment may also be carried out by placing a few flakes of boric acid in a test tube, adding three centimeters of methyl alcohol, and then adding half a dozen drops of concentrated H_2SO_4. Heat gently and ignite the methyl borate just at the mouth of the test tube, taking care that the alcohol does not overflow (Figure 175).
The same experiment can of course be carried out on a larger scale by increasing the quantities of reagents and performing a conventional distillation. Liquid methyl borate is then obtained, and a few drops may be ignited to produce the beautiful green flame that characterizes it and that sometimes serves to identify a borate or boric acid.

- While cooling thoroughly, prepare a mixture of 100 mL of methyl alcohol and 100 mL of H_2SO_4 (pouring the acid into the alcohol). Pour this mixture onto 3 teaspoonfuls of MnO_2 placed in a 1-liter flask connected to a conventional condenser. Heat slowly. The contents of the flask foam enormously and gradually change from black to dirty yellow. A flammable solvent having an ethereal odor is thus obtained: methylal, or dimethoxymethane.

- Assemble a reflux apparatus allowing vanadium pentoxide to boil for an extended period in a large excess of ethyl alcohol of at least 94%. It is therefore best to use a flask surmounted by a Vigreux column or a Raschig-ring column, itself surmounted by a condenser cooled efficiently enough to prevent alcohol vapors from escaping from the top. The mixture is thus brought to a boil for at least half an hour. Slightly unstable vanadium esters then form slowly. When the experiment is stopped, the mixture is allowed to settle and the apparently very faintly colored liquid is collected. If water is added to it, it becomes strongly yellow. This coloration will be darker if the solution has first been strongly cooled

15.3.3 Preparation of Chloroform

As mentioned previously, bleaching powder has almost disappeared from laboratories, although it was long used to prepare chlorine. It can, however, still be employed for an attractive demonstration: the preparation of chloroform.
To do this, freshly prepared bleaching powder should be used rather than material that has been stored for weeks and may have lost some of its effectiveness.
Place in a flask of at least one liter capacity an amount of bleaching powder sufficient to fill a 100 mL beaker. Add 100 to 150 mL of water and then 40 to 50 mL of ethyl alcohol. Connect the flask to a condenser, itself connected to a 100 mL receiving flask through an adapter provided with a gas outlet (see the boxed note on page 441). The flask, resting on wire gauze, is heated gently with a Bunsen burner. As soon as vigorous effervescence is observed, remove the flame. The distillation then continues by itself, although it may occasionally be necessary to reheat the flask for a few seconds by replacing the flame beneath it.
At the same time, prepare a test tube containing a spatula-tip quantity of resorcinol dissolved in a dilute sodium hydroxide solution. To test the product obtained during the distillation, add a little of it to this test tube and heat. The liquid, previously colorless, soon turns pink and then ruby red. This is the test used to identify chloroform.
It is obvious that the product thus obtained is not pure and cannot compete with the commercial material. Furthermore, it is highly uneconomical both in terms of cost and of the time required for its preparation. The experiment described here therefore remains a pure laboratory curiosity.

15.4 Mixtures Without Alcohol

- Place two or three spoonfuls of MnO_2 in a one-liter flask connected to a condenser, then pour in a mixture of 125 mL of lactic acid and 75 mL of HCl. Heat slowly. The mixture begins to foam vigorously, then the reaction subsides and the liquid becomes clearer. Chloral is formed and can readily be recognized by its odor. Good ventilation and the discharge of gases should be provided.

- Assemble a leak-tight ground-glass apparatus consisting of a large flask surmounted by a Vigreux column leading to a condenser and a small receiving flask. An adapter provided with a gas outlet is fitted to the receiving flask (see the boxed note on page 441). Place in the flask a mixture consisting of approximately equal parts of starch (or sugar), MnO_2, and finally dilute HCl (about 25%). The acid may be added at the beginning of the experiment through a stopcock funnel fitted either to a side neck of a two-neck flask or to a double adapter attached to the neck of the flask. Heat slowly. A strong evolution of chlorine first occurs. The mixture then foams heavily, which makes it necessary to use a large flask containing only a small amount of material. When the evolution of chlorine slows down and the mixture becomes hot, chloral, with its charasteristic odor, passes into the condenser.

- In a one-liter flask, mix 1 part of starch or sugar with 4 parts of MnO_2 and 4 parts of water. One may work, for example, with 10 g parts. Heat to 40°C and then allow H_2SO_4 to flow in slowly. The temperature then rises sharply and the mixture foams vigorously. Little by little, various products distill over, including formic acid. Heat gently if necessary after the equivalent of 3 parts of H_2SO_4 has run from the addition funnel.
Some authors recommend mixing from the outset approximately 1 part starch, 4 parts MnO_2 , and 3 parts H_2SO_4 diluted with its own volume of water, then heating gradually. This amounts to the same thing as the previous procedure, except that in the first case the mixing of H_2SO_4 with H_2O automatically causes the temperature to rise. Because of the large evolution of gas, it is important in both cases to provide a reaction flask whose volume is far greater than that of all the substances it contains.

- Into a 2-liter flask fitted with two ground-glass necks, or a single ground-glass neck surmounted by a double adapter, pour a mixture of 150 mL of water and 37 g of potassium dichromate (not all of the dichromate will dissolve). Separately, prepare a mixture of 38 g of 90% ethyl alcohol and 50 g of H_2SO_4 while cooling vigorously. Allow this mixture to cool and place it in a stopcock funnel fitted to one of the flask necks or to one branch of the adapter. On the other neck or branch of the adapter, fit a bent adapter leading to a vigorously cooled condenser. Allow the entire contents of the funnel to run into the flask in a single operation, but not too rapidly. If the temperature does not rise quickly, heat very briefly.
WARNING: The reaction generally runs away, which is why a large flask must be used. Acetaldehyde having a very strong vinegar-like odor distills over.

- Place a mixture of equal parts oxalic acid and glycerol in a distillation flask. Heat. At 75 °C, CO_2 is evolved. At 90°C, formic acid begins to distill. When no more CO_2 is evolved, additional oxalic acid may be added. At the outlet of the condenser, fit the adapter normally intended for vacuum work (see the boxed note on page 441). Through the outlet theoretically intended for connection to a vacuum aspirator, the evolved gas is collected and led into limewater, which becomes cloudy.

- In a distillation flask, mix glycerol with dilute sulfuric acid and add a little manganese dioxide. Distill. Formic acid passes over and can be recognized by its odor.
Concentrated hydrochloric acid may be used instead of dilute sulfuric acid.

- Introduce 5 g of salicylic acid and 7 mL of acetic anhydride into a small 100 mL flask. Place the flask in a water bath maintained between 60 and 70 °C and heat under reflux for a good half hour. The flask is surmounted by a straight air condenser or a straight water condenser (in the latter case operated intermittently). Oily droplets gradually appear on the wall of the flask. Then add 60 mL of water and filter. When placed in ice water, the liquid deposits fine crystals of acetylsalicylic acid (the principal constituent of aspirin).
Here is a somewhat different method for obtaining the same substance...
Take a 200 mL flask fitted with a reflux condenser. The flask is immersed in a

60–70 °C water bath placed on a heated magnetic stirrer. Place 10 g of salicylic acid and 15 mL of acetic anhydride in the flask. When the water bath reaches 60 °C, add 1 mL of concentrated sulfuric acid through a second neck of the flask using a pipette. Heat for 20 to 25 minutes while stirring continuously. Then remove the flask from the water bath and place it back on the stirrer, inserting an insulating piece of cardboard between the flask and the hotplate. Through the upper end of the condenser, immediately add 10 mL of water at room temperature, increase the stirring rate, and wait until the temperature of the flask has fallen considerably. Then add, again through the upper end of the condenser, 50 mL of nearly ice-cold water. An abundant quantity of white crystals of acetylsalicylic acid forms very rapidly. Transfer these crystals to a crystallizing dish or a Büchner funnel, remove as much liquid as possible, then dissolve the crystals in 90% alcohol before allowing them to crystallize again with gentle heating.

15.5 Extraction of Essential Oils

Modern safety standards have led many schools to propose very simple experiments dealing with the extraction of certain essential oils. Most often, clove oil is selected. To obtain it, 25 g of cloves are crushed in a mortar and placed, together with 200 mL of water, in a 500 mL flask fitted with a condenser. The mixture is distilled and between 100 and 130 mL of a cloudy liquid, composed mainly of water, are collected. This liquid is poured into a separatory funnel, and 50 to 70 mL of a saturated NaCl solution are added. The funnel is stoppered and shaken vigorously several times, taking care after each shaking to open the stopcock while the outlet stem is directed upward. This operation, known as salting out, is intended to begin the separation between the water and the essential oil, the latter being only very slightly soluble in salt water. Cyclohexane is then added, the funnel is shaken as before, allowed to settle, and the organic phase containing eugenol, that is to say clove oil, is collected. Very often the demonstration stops at this point, whereas a second distillation, this time fractional and carried out with a Vigreux column (or a similar column), would be required to separate the essential oil from its solvent. And all this merely to obtain, in general, a few drops of pure essential oil...

In other cases, thyme, rosemary, or even orange or lemon peels are used. Here is an example...

-Using a blender, reduce the peels of at least half a dozen mandarins immersed in water to a fluid paste and place them in a flask or an Erlenmeyer flask of at least 1 L capacity, adding more water to obtain a syrupy liquid. By distilling with a Vigreux column and a conventional condenser (straight or vertical), half of the original liquid is collected and poured into a separatory funnel. A little salt (sodium chloride) is added, the funnel is stoppered, and it is shaken while inverted so that the stopcock is located at the top in the open position. A thin, highly refractive liquid layer quickly floats on the surface as soon as shaking is stopped and the mixture is allowed to

stand. Using the stopcock, the two liquids are separated. The refractive layer consists of mandarin essential oil. The quantity recovered is so small that this experiment should be regarded as a pure laboratory curiosity, although it may of course be carried out with other citrus peels. With results that are no more remarkable!

Some teachers also use black mustard seeds, which are first crushed in a mortar, mixed with water, and then left to stand for several hours. Under the action of an enzyme, various chemical reactions occur. Distillation is then carried out using a Vigreux column. Mustard essential oil is thus obtained, namely allyl isothiocyanate, a colorless liquid that causes tearing of the eyes. Care should be taken not to spill it on the hands, as this substance produces inflammation of the skin.

Need it be said that such experiments arouse little interest among high-school students?

A recent trend, inspired by the return to natural products and alternative medicine, now encourages a number of people to undertake the extraction of natural essential oils without really knowing what equipment and conditions are required to obtain results that demonstrate genuine profitability. The most important fact these people seem to ignore is the enormous quantity of plant material that must be gathered in order to obtain 25 mL or more of essential oil. Consequently, planning to work with a one-liter flask is a fundamental mistake. Some believe they can solve the problem by purchasing an expensive 5-liter borosilicate-glass flask. This is another mistake, since such a flask cannot be heated with a simple tripod and Bunsen burner. In order to distribute the heat properly over its surface, a heating mantle, an electric sand bath, or an electric water bath must be used. To regulate the heat correctly, all of these require a laboratory jack that allows the heat source to be lowered when necessary in order to remove the flask from the heat input. When one considers the cost of such heating equipment and of a laboratory jack capable of supporting it, it quickly becomes apparent that this is no longer simple amateur work.

Common sense therefore recommends that amateurs tempted by this "adventure" should use not a set of accessories intended for large chemical laboratories, but rather specialized metal equipment (generally made of copper) designed for distillers. This is certainly not amateur equipment either, but it can often be found at reasonable prices, especially on the second-hand market.

15.6 The Chemistry of Perfumes

From the extraction of plant essences to the manufacture of perfumes there is obviously only one step, and that step appears all the easier when one is unfamiliar with what perfume chemistry actually involves. To gain some idea of it, one may take advantage of a trip to Grasse, near Cannes (France), and visit one of the

(simulated) laboratories presented to tourists by certain major perfume brands. The sight of the equipment and techniques involved, as well as the quantities of plant material required, should be sufficient to discourage simple amateurs and thus spare them many disappointments.

15.7 Preparation of Chromyl Chloride and its Reactions

Chromyl chloride (CrO_2Cl_2) is a liquid inorganic compound that fumes in air and is prepared in a manner somewhat similar to a conventional distillation, which is why it is discussed in the present chapter.

First, an intimate mixture consisting of 10 parts NaCl and 15 to 17 parts potassium dichromate, both previously ground in a stone or porcelain mortar, is heated in a porcelain crucible. Heating must be continued until the mixture melts. Attention should be paid to the preliminary crackling, which may project fine hot particles. To avoid this inconvenience, the crucible may be covered with a fine wire screen. Once the mixture has liquefied, it is heated for a short additional time and then allowed to cool. A compact brownish-red mass is thus obtained and must be broken into pieces. Since these pieces keep perfectly well when dry, it is useful to keep a certain quantity in reserve in a glass bottle.

When chromyl chloride is required, several of these pieces are introduced into a two-neck ground-glass flask, one neck of which is connected to a condenser leading to a receiving flask fitted with an adapter provided with a gas outlet (see the boxed note on page 441). The second neck receives a stopcock funnel containing concentrated H_2SO_4. The entire apparatus must be free of moisture and made of glass with PTFE joints, since no rubber or silicone connection can be used.

An excess of concentrated H_2SO_4, relative to the weight of the pieces employed, is allowed to flow into the flask. Dark red chromyl chloride, almost black and very similar in appearance to liquid bromine, begins to evolve immediately, but slight heating is required to increase its evolution and cause it to distill. It is collected in a flask immersed in an ice-water bath and protected from air, with which it fumes heavily. The receiving flask is finally closed with a ground-glass stopper fitted with a PTFE seal. Chromyl chloride is subsequently handled by means of a glass pipette or, failing that, a polyethylene pipette, although the latter will rapidly turn black and thereafter become unusable.

A simpler method, though in my opinion less reliable, consists of pouring the acid directly onto a homogeneous mixture of 8 parts dichromate and 5 parts NaCl. I consider this method less reliable because the salt mixture inevitably contains some water and is therefore not truly homogeneous.

Chromyl chloride may also be prepared by allowing concentrated H_2SO_4 to flow dropwise into a concentrated hydrochloric solution of CrO_3. But it is, in my opinion, an expensive laboratory curiosity.

WARNING: When the reaction is complete, the various parts of the glass apparatus must be disconnected and immediately immersed in a large container of water. See below for the reaction that occurs with water.

CHROMYL CHLORIDE SOLUTION

Although it is not possible to obtain an aqueous solution of chromyl chloride, it should nevertheless be known that it is soluble in chloroform, which may sometimes make it possible to moderate the violent reactions that it can produce...

- Upon contact with water, chromyl chloride decomposes into a mixture of chromic acid and hydrochloric acid. If additional water is added, a blue coloration appears, the chromic acid then becoming perchromic acid. If SO_2 is bubbled through the solution, a green-violet color is obtained because chromium sulfate is then formed.

- Chromyl chloride is cautiously poured into ammonia or a NaOH solution. The color becomes golden yellow owing to the formation of ammonium chromate or sodium chromate, both of which produce a yellow precipitate in an aqueous solution of lead acetate.

- Pour 2 cm of ether into a long test tube and then allow a few drops of chromyl chloride to fall into it. The reaction is very vigorous and accompanied by flames. Abundant greenish-yellow fumes are evolved (Figure176).

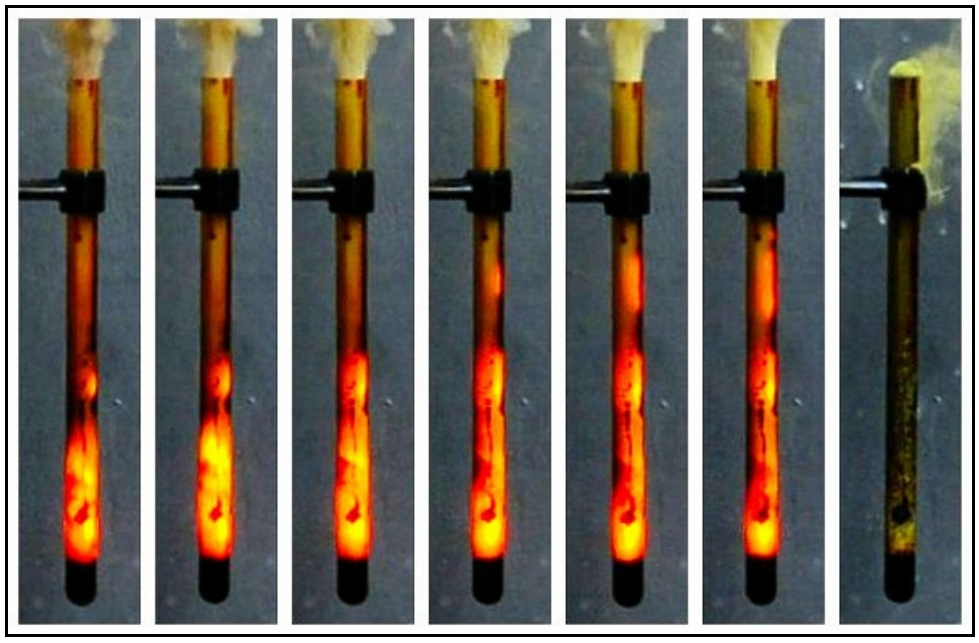


Figure 176

A similar but less vigorous reaction may be obtained by using aceton instead of ether.

- Prepare two test tubes, the first containing a few centimeters of a potassium bromide solution and the second a few centimeters of a potassium iodide solution. Into each, add one or two drops of chromyl chloride. Depending on the case,

bromine or iodine is liberated, which can be verified simply from the color obtained by pouring two or three drops of these solutions into a little chloroform.

- Pour liquid chromyl chloride into a relatively concentrated solution of potassium chromate. A chlorochromate precipitate immediately forms. It is said that the addition of acetic acid to the original solution is necessary, but I did not find this to be useful.

- Pouring two drops of chromyl chloride into a nitric acid solution of mercuric nitrate immediately produces a beautiful yellow precipitate of mercuric chromate.

- In a series of seven porcelain dishes, place respectively a small quantity of urea, a small quantity of camphor, a small quantity of sulfur, a small quantity of mercury, a small amount of ethyl alcohol, and a small amount of turpentine. Into each dish, allow two to four drops of chromyl chloride to fall. In every case, a vigorous reaction occurs with the production of abundant fumes that should not be inhaled. The reaction is particularly vigorous with sulfur and with turpentine, the latter producing a small explosion and flames upon contact with each drop of chromyl chloride. The alcohol may sometimes ignite. Depending on the substance used, brownish or greenish residues are obtained, generally insoluble or only slightly soluble in water. With mercury, the reaction is vigorous and persists for a long time. In that case, the residue is completely soluble in water.
If, instead of pouring liquid chromyl chloride onto the urea, chromyl chloride is brought into contact with it in the gaseous state, the urea appears to melt into a colorless liquid. Subsequently, when exposed to air, this substance becomes greenish-yellow and yields a green solution in water.

- Place a little hydrogen peroxide in a Drechsel bottle or even in a simple beaker. Slowly pass uncooled chromyl chloride vapors through it. The liquid becomes green and gradually shifts toward blue (Figure 177).

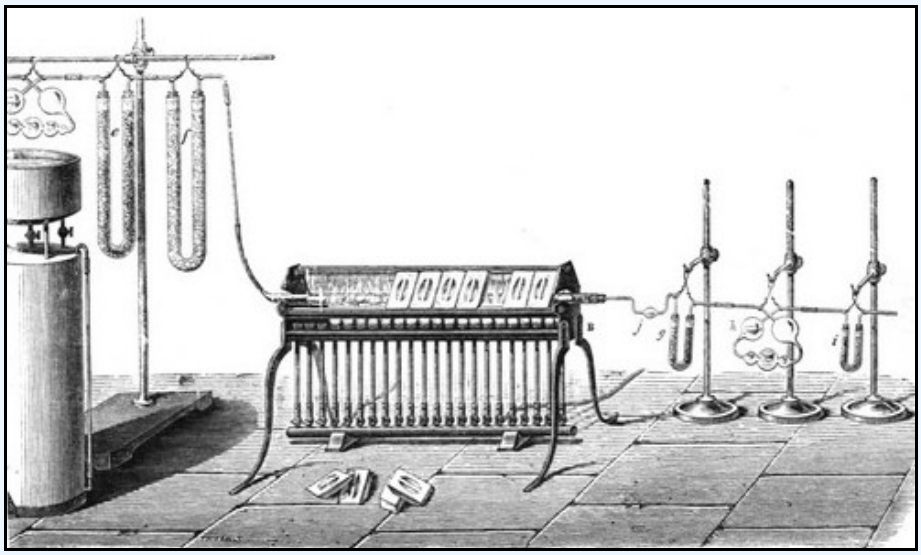
Figure 177

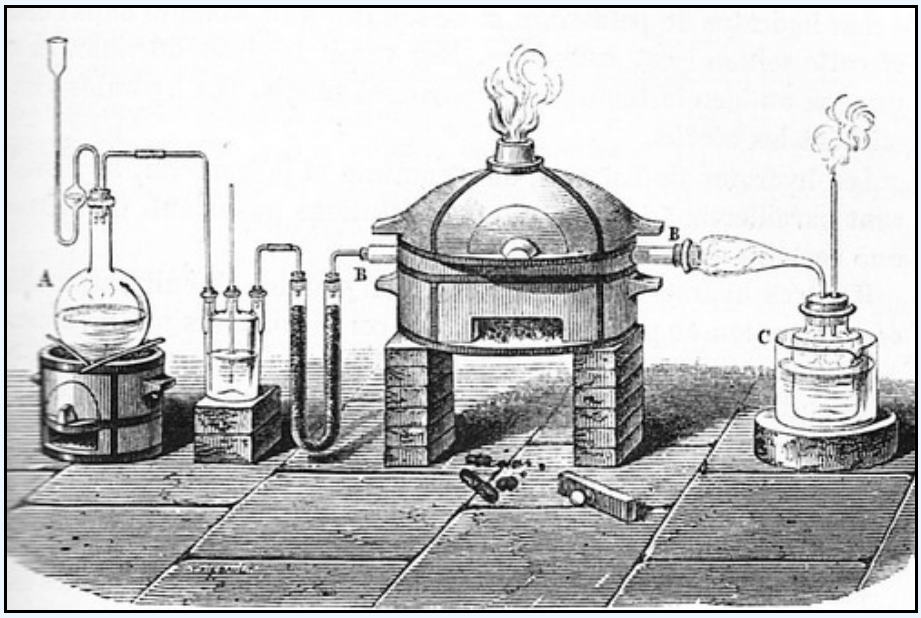
- Place a piece of yellow phosphorus about the size of half a pea in a porcelain or refractory earthenware dish. Position above it the outlet tube from a chromyl chloride apparatus. Upon reaching the phosphorus in gaseous form, the chromyl chloride causes it to warm and melt. The phosphorus then gradually burns, producing small white vapors. This experiment must be carried out outdoors because of the toxicity of the substances involved. Liquid chromyl chloride must never be used for this experiment because of the danger of explosion and splashing.
- The formation of chromyl chloride may be used as a test for chlorides in the solid state. To do this, the solid substance is ground in a mortar with a little potassium or sodium dichromate, after which the mixture is placed in a test tube and sulfuric acid

is added. The tube is heated and one observes whether a red gas appears. If so, the unknown substance contains a chloride.

A LITTLE HISTORY...

Types of laboratory utensils and experimental setups in use in the 19th century and still in use into the early 20th century





(A. D. Wurtz, Leçons élémentaires de chimie moderne, Paris: Masson, 1894.)

Chapter 16 - Heating Solids

16.1 Metals and Nonmetals

Sodium

- Some chemists claim that sulfur and sodium combine even at room temperature. I have never observed anything of the kind. When heated, however, the reaction is violent. Place a small piece of sodium on a bed of powdered sulfur in a small porcelain crucible and heat it gently from below. The sulfur first melts and the sodium settles into it until a flame suddenly appears.
WARNING: Within only a few tenths of a second, the temperature becomes high enough to shatter the crucible. Consequently, this experiment should be carried out only with very small quantities of material, outdoors on a concrete surface, while standing two or even three meters away (Figure 178).

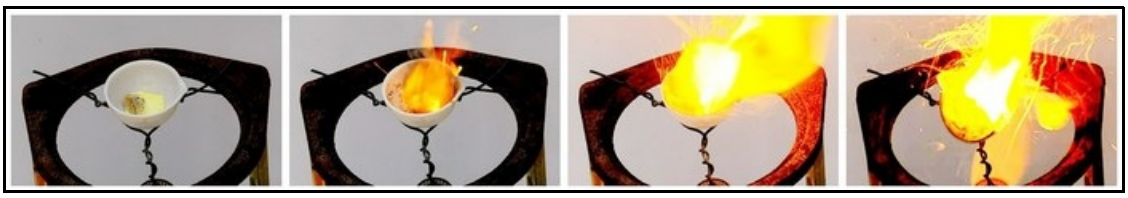


Figure 178

After the reaction has finished, thoroughly flood the area with water to ensure that no unreacted sodium particles remain.

- In an ordinary borosilicate glass test tube, place a piece of sodium about the size of a pea together with an equal-sized piece of chromium trioxide. Clamp the tube to a metal stand outdoors and heat it with a torch flame. At first, a few white fumes appear, then suddenly an intense yellow flame.
WARNING: material may be ejected from the tube. Allow the tube to cool. Then, very cautiously (since some sodium may remain), add water. The liquid turns

yellowish-green owing to the presence of finely divided chromium oxide.

Iron

- Heat a mixture of iron powder and ammonium chloride in a large test tube. White fumes are evolved, the odor of ammonia becomes noticeable, and a thin yellow deposit forms on the cooler part of the tube. Stop heating, dilute the contents with water, then add a sodium hydroxide solution. A green precipitate of iron(II) hydroxide forms because iron(II) chloride had previously been produced.
Repeat the experiment using zinc powder. This time, the deposit is white rather than yellow.

- Place a mixture of flowers of sulfur and iron powder on a firebrick. Touch it with a steel wire heated to red heat. The mixture generally ignites and is converted into iron sulfide. This is a classic experiment presenting little danger.

- Place a mixture of 5 g of iron powder and 10 g of potassium nitrate in a crucible. Heat strongly until it melts. Pour the melt into water. The solution becomes red. Potassium ferrate has been formed. Sometimes the water first turns green before finally becoming red. Potassium ferrate is unstable in water and rapidly decomposes into ferric hydroxide.

- Heat an intimate mixture of iron powder, sodium nitrate, and sodium hydroxide in a test tube. Insert a moistened pH indicator paper into the mouth of the tube. A strongly alkaline gas is evolved, and white fumes appear when an open bottle of hydrochloric acid is brought close to the tube. The gas is ammonia.

- Place a little iron powder together with an equal quantity of powdered chromium trioxide in a small test tube about 8 mm in diameter. Mix the powders and heat them. A fairly vigorous reaction occurs, and the test tube is usually destroyed.

- Ferrocerium is an alloy composed of several elements, mainly iron, cerium, lanthanum, neodymium, and others. Better known as the material used in lighter flints, it is generally supplied as small rods about 4 or 5 mm long. When scraped against a hard, rough surface such as certain paving stones or concrete, these rods produce sparks. They may also be heated to red heat beforehand. In that case, glowing particles detach themselves and remain red-hot for quite some time. An even more spectacular experiment consists of heating one of these rods to red heat while holding it with metal tongs, then dropping it onto a hard surface. It bursts into a shower of sparks.

Copper

- Mix copper powder and flowers of sulfur in approximately equal proportions, using

a slight excess of sulfur. Place the mixture on a porcelain combustion boat. Heat one end. A flame appears and rapidly spreads throughout the entire mixture, which becomes black and compact. Copper(II) sulfide (CuS) has been formed (experiment already described earlier).

The reaction between copper and sulfur may also be carried out as follows. Pour 3 or 4 cm of powdered sulfur into a test tube, then insert a copper wire into it. Heat the tube. As soon as the sulfur vapor reaches the copper wire, it first glows red and then turns black (Figure 179). After cooling, simply immerse the blackened portion of the copper wire in hydrochloric acid. The characteristic rotten-egg odor of hydrogen sulfide is immediately detected.

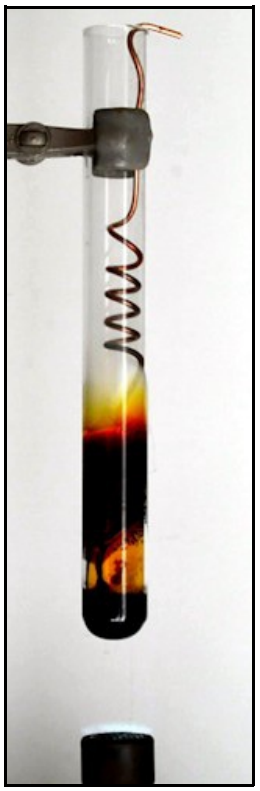


Figure 179

Very curiously, the combination of copper and sulfur can also be achieved at room temperature. Prepare a solution of sulfur in carbon disulfide in a small tightly stoppered bottle. Place one drop of this solution on a sheet of copper and allow it to evaporate. As the carbon disulfide evaporates, it leaves behind a black layer of copper sulfide. This layer disappears immediately when immersed in hydrochloric acid, producing the characteristic rotten-egg odor.

- Heat a heavily oxidized piece of copper to red heat, then press it into ammonium chloride. The copper is almost instantly restored to a bright metallic surface.

Zinc

- Place zinc granules in a steel crucible and heat them with a Meker burner. At 420 °C, the zinc melts. Continue heating. At a higher temperature, while stirring with an iron rod, small ignitions and slight white fumes of zinc oxide are observed. If the temperature can be raised to about 920 °C with the aid of a portable torch, the zinc ignites and volatilizes, producing a dense white cloud of zinc oxide.

- In a small crucible, mix approximately equal amounts of powdered sulfur and a slight excess of zinc powder. Add a trace of copper powder. The total quantity must never exceed about 2 cm^3. Place the mixture in a covered porcelain crucible fitted with a vent hole and heat it. Suddenly, a large flame appears and the crucible may shatter. An impure zinc sulfide is formed. After prolonged exposure to sunlight, it may become luminescent in the dark and under ultraviolet light. Collect it from the walls of the crucible, where it adheres.
WARNING: This experiment is therefore hazardous, and it is important to remain well away from it while adequately protected.

- Reduction of an intimate mixture of zinc powder and titanium dioxide heated in a test tube proceeds with incandescence.

- Heat a homogeneous mixture of zinc powder, iron powder, and a few pellets of potassium hydroxide in a relatively narrow test tube. Hydrogen is evolved. It may be ignited.

- Place in a crucible an intimate mixture corresponding to about one teaspoonful of silica powder and zinc powder. Heat it to a temperature well below 100 °C, then pour 2 or 3 mL of carbon tetrachloride onto it. Dense, suffocating white fumes are immediately produced. This experiment must be carried out outdoors.

- In a small test tube about 10 cm long and 6 mm in diameter, prepare a 1:1 mixture of zinc powder and calcium hydroxide. Heat strongly. As soon as gas evolution begins, bring the mouth of the tube into a flame. The characteristic barking sound of hydrogen mixed with a little air is heard. Hydrogen, calcium oxide, and zinc oxide have in fact been formed. Allow the tube to cool, then add water. A considerable rise in temperature is observed as the water reacts with the quicklime.

- In a borosilicate glass test tube having an internal diameter of approximately 18 mm and held vertically, place a 3 cm strip of zinc in a layer of 12 to 15 mm of dry ammonium nitrate. Heat until the nitrate has completely melted, at which point it begins to react with the zinc. Immediately remove the flame to avoid any danger of explosion. The reaction rapidly becomes violent and evolves a large amount of heat. Nitrogen mixed with zinc oxide produces dense fumes. To obtain an even more vigorous reaction, some authors recommend adding a little ammonium chloride to the original ammonium nitrate–zinc mixture. Depending on the quantities used and the heat generated, a small explosion accompanied by a considerable evolution of reddish-brown fumes may eventually occur. Figure 180 shows the course of this experiment: first the fumes appear, then the mass becomes yellow. Next, the white fumes cease, but the reaction continues and the mass becomes increasingly yellow until a jet of reddish-brown vapors escapes in a small explosion.
A similar reaction is even capable of attacking gold and platinum.

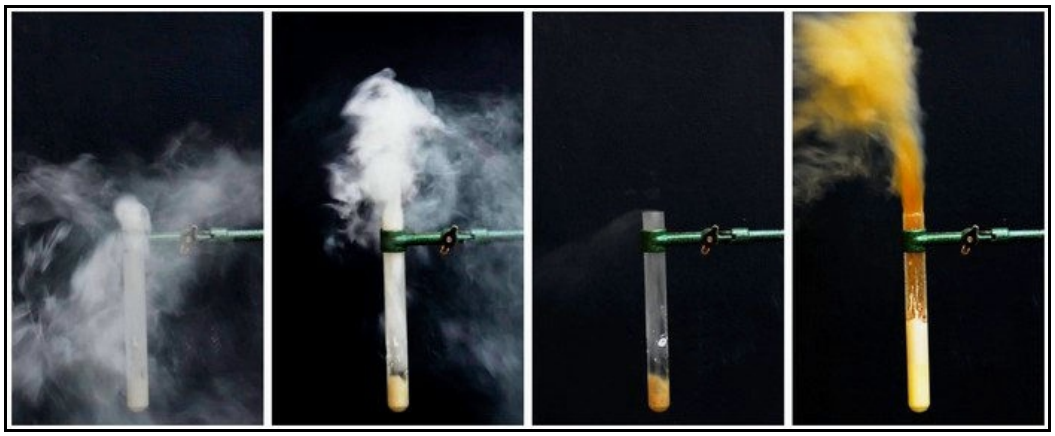


Figure 180

- If a mixture of arsenic trioxide and twice its amount of zinc powder is heated in a micro test tube, a violent reaction occurs that may be dangerous. After cooling,

bright metallic arsenic can be seen inside the irrecoverably damaged tube. The same experiment may be attempted by replacing arsenic trioxide with mercury sulfide, although the result is much less conspicuous.

- Heat a mixture of mercury sulfide and zinc powder in a small test tube. A strong incandescence is observed. Allow the tube to cool. Mercury is found to have volatilized and condensed on the walls of the tube. Only very small quantities should be used, since the reaction may be explosive.

- A mixture of zinc powder and manganese chloride explodes when heated. It should therefore be carried out only with a very small quantity of material in a sacrificial micro test tube (5 to 7 mm internal diameter and 5 to 8 cm long).

Lead, Tin

- Melt lead or tin in a crucible placed outdoors. Once the metal is molten, add a generous quantity of flowers of sulfur. The reaction is vigorous and produces abundant sulfur dioxide fumes. The remaining black material consists of lead sulfide or tin sulfide, which can easily be identified by the characteristic rotten-egg odor released when a fragment is placed in hydrochloric or sulfuric acid.

- Heat a mixture of small pieces of tin and an excess of iodine in a porcelain crucible. Ignition occurs, a large amount of iodine vapor is evolved, followed by yellow fumes. Stop the experiment at this point. After cooling, a yellowish solid of tin iodide is found in the crucible. Because of the iodine vapors produced, this experiment must be carried out outdoors with your back to the wind.

Magnesium

- Mix intimately 4 g of calcium phosphate with 2 g of magnesium powder in a porcelain crucible. Heat the uncovered crucible on a tripod while standing 2 to 3 meters away. The objective is to reduce the calcium phosphate to calcium phosphide, which reacts with water to produce phosphine. It is advisable to tilt the crucible slightly so that its opening faces away from the observers. After the mixture has swollen slightly, a bright incandescence usually develops, indicating the formation of calcium phosphide and magnesium oxide. In my own experiments, however, I observed a powerful explosion that hurled the entire contents of the crucible several meters away. This experiment must therefore never be attempted with larger quantities of material.
Alternatively, first prepare a calcium phosphate precipitate by mixing, for example, ammonium phosphate and calcium chloride solutions. Dry the precipitate rapidly and mix it with fine magnesium filings. Place the mixture in a crucible and heat it. Red-glowing spots appear throughout the mass. The phosphate is reduced, forming calcium phosphide and magnesium oxide.

After cooling, fill the crucible with water using a wash bottle. Bubbles of phosphine are evolved, accompanied by its characteristic garlic-like odor. As a reminder, phosphine must never be inhaled under any circumstances.

– In a porcelain crucible, heat magnesium powder with a large excess of boric acid. Bluish fumes are observed. The mixture eventually becomes a gray solid. This is magnesium diboride (MgB_2), which is insoluble in water and has various industrial applications but none in an amateur laboratory. The crucible may be cleaned first with hydrochloric acid and then with aqua regia.

- Cut a magnesium ribbon into small pieces and place them together with mercury in a test tube. Heat the tube. At a temperature below its boiling point, the mercury amalgamates with the magnesium, producing a clearly audible sound. Allow the tube to cool, then add water with a wash bottle. A vigorous evolution of hydrogen is observed.

- Take a little green chromium(III) oxide (Cr_2O_3), which is particularly insoluble and resistant to acids. Mix it intimately with fine magnesium turnings. Place the mixture in a sturdy test tube and heat it with a Bunsen burner. At a certain temperature, a brilliant incandescence develops and illuminates the entire mass. Allow the tube to cool, discard the residue consisting of some green chromium oxide and magnesium oxide, which forms a hydroxide identifiable by its pH and its reaction with an acid. Metallic chromium remains firmly attached to the walls of the test tube.

- Reduction of a mixture of magnesium and zinc oxide heated in a borosilicate 3.3 glass test tube proceeds with incandescence.

- Heat one spatula tip of lithium carbonate together with one spatula tip of magnesium powder in a small test tube. After a while, the mixture ignites and the entire mass becomes red-hot. The tube is destroyed, being partly melted by the heat evolved (Figure 181).

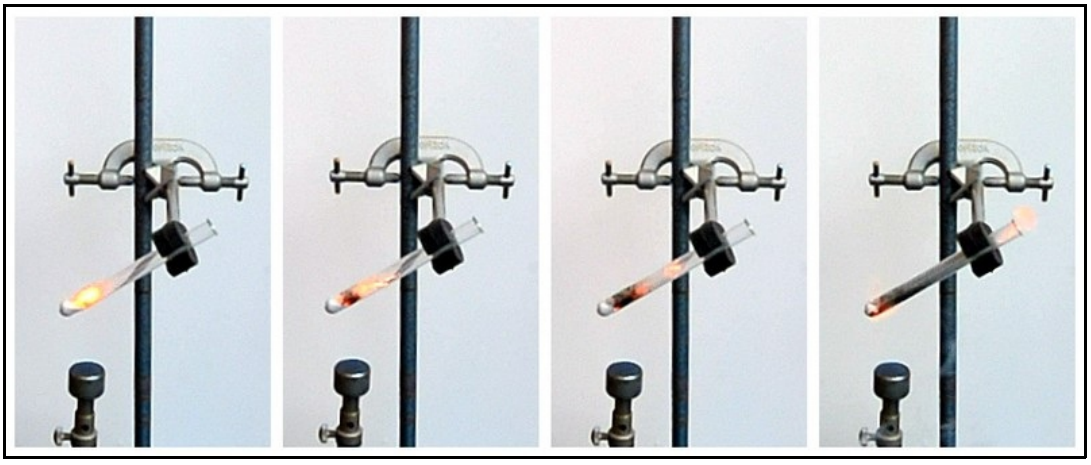


Figure 181

- Place a small amount of CuO together with a little magnesium filings in a miniature test tube approximately 10 cm long and 8 mm in diameter. Heat the tube while keeping it well away from yourself, with its open end directed toward a safe area. Suddenly, a large flame appears. The test tube may become partly melted and distorted. Bright red metallic copper can be seen fused into the glass.

- Place approximately 1 cm^3 of ammonium nitrate in a vertically held test tube and heat it until it melts. At that moment, drop in a strip of magnesium ribbon 2 to 3 cm long. A vigorous reaction occurs. Dense white fumes are evolved together with a strong odor of ammonia.

- This experiment is carried out in two stages. First, in a borosilicate glass test tube (which will be sacrificed), place equal parts of fine white sand (previously washed with hydrochloric acid and dried) intimately mixed with magnesium powder or the thinnest magnesium turnings available. Heat strongly. Incandescence is observed, and the material in the tube turns black.
If diatomaceous earth (kieselguhr) or silica gel is used instead of sand, the reaction is considerably more vigorous, and appropriate precautions must be taken. A large flame may be produced, and part of the material may be projected from the test tube. The magnesium silicide thus obtained is of better quality than that prepared from sand because, with sand, the reaction is far from complete throughout the entire mass.
The second stage of the experiment consists of recovering the magnesium silicide and pouring it into a crystallizing dish containing water acidified with hydrochloric acid. The liquid immediately begins to foam, and small sharp popping sounds are heard, similar to those produced by sodium burning on the surface of water. The silicide reacts vigorously to form magnesium chloride and silane (SiH_4), also known as silicon hydride. This impure silane is spontaneously flammable.
Another way to perform the second stage of this experiment is to place the silicide in a fairly small two-neck round-bottom flask fitted with ground-glass joints, one connected to a dropping funnel and the other fitted with a simple outlet tube. This time, concentrated hydrochloric acid is placed in the funnel and allowed to enter the flask one drop at a time, intermittently. The acid must never be allowed to flow continuously because each drop produces a small explosion accompanied by a flame. A dense plume of smoke emerges from the outlet tube.

- Mix a small quantity of powdered copper sulfate with magnesium powder and heat the mixture, preferably in a small crucible covered with its lid. A very violent explosion occurs. The crucible shatters into numerous fragments, each coated with a dark substance that should be copper but is probably copper oxide.
WARNING: This experiment is very dangerous and requires appropriate protection.

- In a small test tube, mix a pea-sized quantity of lithium carbonate with an equal quantity of magnesium powder. Heat the mixture. The mass suddenly ignites, and upon cooling the test tube becomes cracked and may even appear distorted because of the strongly exothermic reaction.

- The hot reduction of molybdenum trioxide by magnesium is explosive. It must be carried out in a micro test tube 5 to 6 mm in internal diameter and approximately 10 cm long. Place one lancet-tip measure of magnesium powder in the tube, followed by an equal quantity of molybdenum trioxide. Heat while keeping the mouth of the tube pointed away from everyone and standing well back. A violent flame at least 3 cm long suddenly appears, and the tube is destroyed, its surface becoming covered with bubbles and cracks because of the intense heat generated.

- Heating a mixture of magnesium powder and calcium carbide powder in a test tube produces incandescence accompanied by white fumes. Magnesium carbide (Mg_2C_3) is most probably formed. With water, it can produce acetylene, although in a smaller amount than calcium carbide. However, when treated with water acidified with hydrochloric acid, sparks are produced, just as with magnesium silicide (see page 461).

Aluminum

- According to certain chemistry books, it is sufficient to mix aluminum powder with iodine and then add a few drops of water to obtain a reaction forming aluminum iodide. I found that slight heating is also required. If the aluminum iodide is to be preserved, an excess of iodine should be used. The reaction is almost instantaneous and produces a dense cloud of iodine vapor (Figure 182).

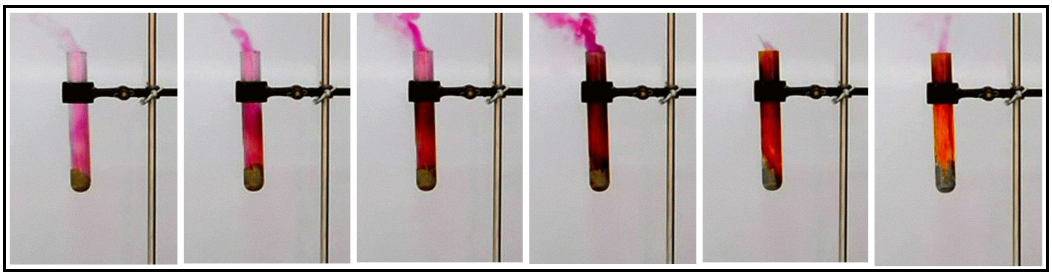


Figure 182

- In a porcelain dish, heat with a very hot flame an intimate mixture of aluminum powder and either animal charcoal or very finely powdered retort carbon. The mixture becomes slightly brown. Aluminum nitride has formed, the metal having absorbed both oxygen and nitrogen from the air. After cooling, transfer the powder to a small flask containing a concentrated sodium hydroxide solution. Vigorous foaming occurs, and moist indicator paper reveals the evolution of ammonia. Nessler's reagent may also be used.

- Heat an intimate mixture of aluminum powder and red phosphorus in a small crucible. The mixture eventually ignites, producing abundant white fumes. Solid aluminum phosphide reacts only slowly with water, producing small bubbles of phosphine.

- Heat an intimate mixture of flowers of sulfur and aluminum powder to red heat in a porcelain crucible fitted with its lid. Allow it to cool in a very dry place. The product obtained is gray. Detach it from the crucible using the point of a dissecting needle, repeatedly driving it into the mass. Then immerse the material in water. Vigorous foaming begins, accompanied by the characteristic rotten-egg odor, while hydroxide remains behind. Aluminum sulfide therefore does not keep in moist air, where it slowly decomposes with the evolution of hydrogen sulfide. It must therefore be stored in airtight bottles.

- Heat a little selenium together with aluminum powder in a test tube. A vigorous reaction occurs, producing a very bright flame somewhat resembling that of burning magnesium. Allow the tube to cool, then add water. The aluminum selenide that has formed reacts to produce hydrogen selenide (hydroselenic acid), a gas with an odor somewhat similar to hydrogen sulfide but far more toxic and therefore extremely dangerous to produce except in minute quantities and in a very well-ventilated room, or preferably outdoors. The reaction between powdered selenium and powdered aluminum may also be initiated with a red-hot iron rod. Incidentally, it should be noted that the combination of selenium with iron is much less readily obtained, and the selenide formed reacts only with hydrochloric acid.

Chromium, Titanium, Tungsten, Molybdenum

- Heat potassium chlorate gently in a test tube containing a strip of chromium. When the chlorate melts and begins to foam, it reacts vigorously with the chromium, producing an orange substance while a yellowish-green gas is evolved. Upon cooling, the orange color changes to canary yellow. This substance dissolves in water. Upon addition of hydrochloric or sulfuric acid, the color becomes darker. This is a characteristic property of chromates (Figure 183).

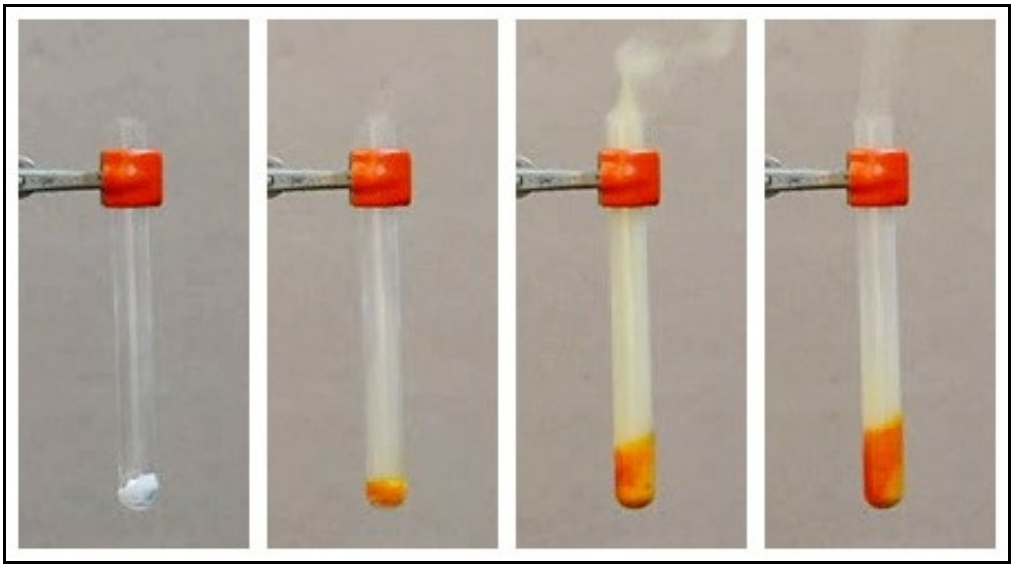


Figure 183

- When heated with a few pellets of sodium hydroxide, chromium powder reacts with the evolution of hydrogen. After cooling, the residue gives a yellow solution of sodium chromate when water is added.

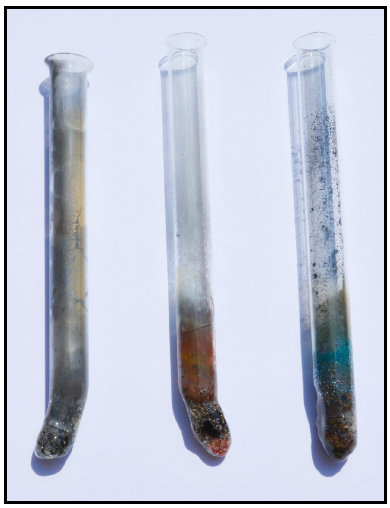


Figure 184

- Place a layer approximately 5 mm deep of titanium powder into each of three small test tubes about 8 mm in diameter. Add an equal quantity of lead(II) oxide (PbO) to the first tube, an equal quantity of CuO to the second, and an equal quantity of potassium permanganate to the third. Mix each tube by shaking, then heat them individually with a torch. A very violent reaction, accompanied by flame and incandescence, occurs in each tube, the heat being sufficient to melt part of the glass. From left to right in Figure 184 are shown the tubes containing PbO, CuO, and $KMnO_4$. The yellow, red, and blue colors correspond to the different metals or their oxides.

- If titanium powder is intimately mixed with flowers of sulfur and placed on a ceramic surface, simply touching the mixture with the tip of a torch flame is enough to make it burn.

Figure 185

- If titanium powder is intimately mixed with red phosphorus and arranged as a thin ribbon in a porcelain dish, touching it with the tip of a torch flame is sufficient to make the mixture burn while producing abundant white smoke (Figure 185).

- In a small crucible, mix equal parts of titanium powder and sodium hydroxide pellets. Cover the crucible and heat it with a Meker burner. At one point, a large flame caused by burning hydrogen may emerge around the edge of the lid. A black mass remains in the crucible.

- Place a few sodium hydroxide pellets in a small porcelain crucible and mix them with a little tungsten powder. Heat gradually. The sodium hydroxide melts and the mixture foams rather vigorously. When the foaming stops, continue heating briefly, then allow it to cool. Add a little water and dissolve the gray residue with a glass rod. Filter the mixture. The alkaline filtrate contains a small amount of sodium tungstate. Add two drops of hydrochloric or sulfuric acid. A slight white precipitate of tungstic acid appears. Then add one lancet-tip measure of zinc powder. A beautiful blue coloration develops owing to the formation of tungsten(V) oxide (W_2O_5). By contrast, mixing sodium tungstate with a nitric acid solution of mercuric nitrate produces a yellow precipitate.

- Mix tungsten powder with an excess of potassium hydroxide in a porcelain crucible and heat the mixture. It melts, a flame appears, and potassium tungstate is formed.

This compound is soluble in water. Potassium tungstate produces various precipitates: pink-lilac with cobalt chloride, dirty yellow with ferric chloride, white with barium chloride, bluish-white with copper sulfate, and so on.

- Place a few sodium hydroxide pellets together with an equal quantity of potassium nitrate in a miniature porcelain crucible. Add one lancet-tip measure of tungsten powder and heat the mixture. A yellowish liquid forms, then becomes colorless and finally solidifies into a white mass upon cooling. Heat a little water in the crucible, then pour the contents into a test tube. Add a few drops of hydrochloric or sulfuric acid. A heavy white precipitate forms.

- Heat a mixture of lead dioxide (PbO_2) and molybdenum powder in a small test tube. The reaction produces an intense light and such extreme localized heat that the test tube is generally shattered (Figure 186).

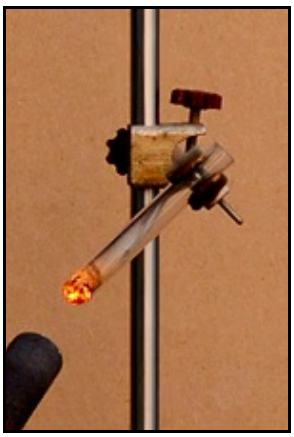


Figure 186

- Place a little molybdenum powder together with powdered potassium permanganate in a test tube that will be sacrificed. Shake to mix, then heat with a torch. A flame suddenly appears. The reaction is violent (Figure 187).

Figure 187

- Place approximately 1 cm^3 of powdered potassium chlorate in a test tube and cover it with a quantity of molybdenum powder about the size of half a pea. Heat the vertically held tube while standing well back. Suddenly, when the chlorate melts, a brilliant white flame together with white smoke is produced (Figure 188).

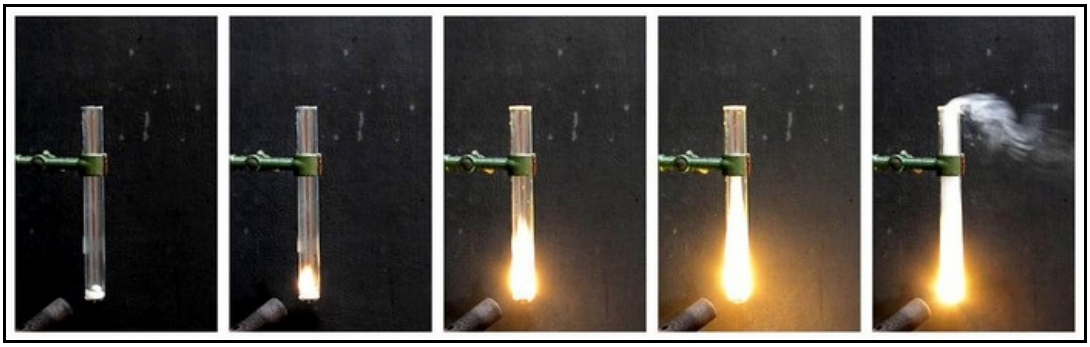


Figure 188

Cadmium

- Pieces of cadmium placed in about 1 cm^3 of ammonium nitrate and heated burn vigorously with white fumes. The remaining material then evolves reddish-brown vapors.

Mercury

Some chemists claim that it is sufficient to boil mercury and pour it onto flowers of sulfur to produce mercury sulfide. This is incorrect. In fact, this reaction can occur in only two different ways...
- Melt sulfur in a crucible, then add a small amount of mercury. The color changes from red to black, and mercury sulfide is immediately formed. Stop heating and allow the crucible to cool. Transfer the solid mass to a test tube and heat it. The sulfur is driven off, leaving mercury behind.
- Mercury and sulfur are placed together in a crucible and heated simultaneously. It should be noted that an excess of sulfur should be used and that it is advisable to stir the mixture with a glass rod as soon as the reaction begins. An impure powdered mercury sulfide can then be obtained by crushing the contents of the crucible.

- First prepare a mercury-tin amalgam by heating 6 parts of mercury with 12 parts of tin. After the amalgam has cooled, break it into small pieces and mix them intimately with 6 parts of sulfur and 6 parts of ammonium chloride. Heat the mixture in a porcelain crucible until the abundant toxic blue fumes cease. If possible, stir from time to time with a glass rod (carry out this experiment outdoors and upwind). The product obtained is the substance formerly known as mosaic gold (stannic sulfide). It has often been written that alchemists once abused the credulity of many people by performing this experiment before them as an apparent demonstration of their skill. I have my doubts about this, however, because it requires quite a vivid imagination to mistake the dull yellow color of mosaic gold for genuine gold!

Antimony

- Some chemistry books state that the reaction between antimony and iodine is extremely vigorous, even dangerous. In fact, it appears to be chiefly highly exothermic, since the test tube I used cracked after part of the iodine had been converted, upon heating, into a reddish cloud. A yellow coloration marked the zone where the two substances combined.

Carbon

- In a straight test tube, heat arsenic trioxide with powdered charcoal. Arsenic is

deposited slightly higher up, in the cooler part of the tube, as a bright ring that dissolves in hot hydrochloric acid.

Sulfur and Selenium

- Melt sulfur in a small short-neck flask that will subsequently be reserved for other experiments involving molten sulfur. While still liquid, pour it quickly into cold water. An elastic sulfur thread is obtained that remains flexible for a short time. This is the variety known as plastic sulfur.

- Heat a small amount of bismuth in a crucible. When it has melted, add a small quantity of sulfur. The mixture is immediately converted into bismuth sulfide, which can subsequently be treated with hydrochloric acid to produce hydrogen sulfide.

- Place an intimate mixture of flowers of sulfur and potassium chlorate in a test tube. The total volume must not exceed 1 cm^3. Clamp the tube in an inclined position and heat its bottom. Very quickly, a flash as bright as burning magnesium is produced. After the tube has cooled, add water, shake, then decant or filter. Divide the resulting solution into two equal portions. Test the first with barium chloride solution and the second with silver nitrate solution. In the first case, a white precipitate is obtained; in the second, a white precipitate rapidly turning violet-black. This demonstrates that a mixture of potassium chloride and potassium sulfate has been formed.

- Melt a small quantity of potassium chlorate in a porcelain crucible after adding a little manganese dioxide to prevent it from exploding. Fusion takes place rather quickly. Drop a small piece of sulfur into the molten salt. It burns with the characteristic violet flame of potassium.

- Place equal quantities of flowers of sulfur and potassium nitrate in a test tube fitted with a bent delivery tube leading into a small amount of water contained in a beaker. Heat slowly (this is important). White fumes begin to evolve and bubble through the water. Be sure that the delivery tube is of wide bore because the reaction soon becomes very vigorous and gas evolution becomes considerable. The test tube remains brightly illuminated by an intense white light (Figure 189), after which the reaction ceases. Using barium chloride solution and a pH indicator, it can be shown that the white fumes consisted of sulfur trioxide, which reacted with the water to form sulfuric acid.

Figure 189

This hazardous reaction was once proposed by the chemist Alfred Morgan as a convenient method for preparing sulfur trioxide in a book intended for amateur chemists (*Simple Chemical Experiments*, New York, Appleton Century, 1941, pp. 57–58). With a certain degree of recklessness, he

merely stated that it was sufficient to heat gently. In fact, it is equally important to work with only small quantities of material!
This experiment may also be carried out in another way. Melt potassium nitrate in a porcelain crucible. Once molten, drop in a small piece of sulfur, preferably rolled into a little ball. The sulfur immediately burns with an intensely bright white flame, somewhat resembling that of burning magnesium. Allow the crucible to cool, dissolve its contents in water, and again verify the presence of sulfate ions with barium chloride.

- Place a mixture of copper sulfate and powdered sulfur, the latter in excess, in a borosilicate 3.3 glass test tube. Heat the mixture. The mass turns black while sulfur vapor and sulfur dioxide are evolved, some of the sulfur condensing near the top of the tube (hence the need to use an excess of sulfur relative to the copper salt). Allow the tube to cool, then add a few drops of hydrochloric or sulfuric acid. A gas is heard to evolve. Its odor identifies it as hydrogen sulfide. Copper sulfide has therefore been formed.

- Mix equal parts of vanadium pentoxide and sulfur in a crucible and heat them. Very quickly, the mixture turns black while foaming slightly. Allow it to cool. The resulting black solid appears powdery. Add a little water, two or three drops of sulfuric acid, and warm gently. A magnificent blue solution is obtained together with a faint odor of hydrogen sulfide. If a few black particles remain attached to the crucible, they may be removed by gently warming with nitric acid. If the blue solution is diluted with water and ammonia is then added, a precipitate is obtained whose color varies from brown to goose-dropping green.

- Heat an intimate mixture of flowers of sulfur and manganese dioxide in a test tube and collect the evolved gas in a stemmed glass containing a potassium permanganate solution. The latter is rapidly decolorized owing to the evolution of sulfur dioxide. Manganese sulfide remains in the test tube and produces the characteristic odor of hydrogen sulfide when treated with hydrochloric acid.

- Heat an intimate mixture of flowers of sulfur and potassium carbonate in a test tube or a crucible. Effervescence occurs. When it ceases, a red solid remains. Early chemists called it liver of sulfur. It is in fact potassium sulfide, which gradually becomes yellow and deliquescent on exposure to air. It evolves hydrogen sulfide when a few drops of hydrochloric acid are added.

- Place about 1 cm^3 of flowers of sulfur together with a somewhat smaller quantity of chromium trioxide in an ordinary test tube. Heat the mixture. The sulfur melts, after which sparks soon appear inside the tube. Finally, the reaction proceeds with a brilliant white light, and the tube becomes coated with a layer of green chromium oxide. Black chromium sulfide remains at the bottom of the tube and reacts with hydrochloric acid. The test tube is generally destroyed.

- Heat together equal portions of sulfur and paraffin in a test tube. A yellow liquid

first forms, within which a separate globule gradually changes from yellow to red. The two liquids then merge into a boiling red liquid while the unpleasant characteristic odor of hydrogen sulfide is released. This odor remains detectable in the test tube even after 24 hours. The tube is destroyed.

- Heat a mixture of selenium and potassium permanganate in a test tube. At a certain point, a brilliant light appears. Selenium dioxide (SeO_2) has been formed. Allow the tube to cool, then add hydrogen peroxide. The pH then indicates strong acidity.

- A mixture of cadmium and selenium placed in a small test tube ignites or produces a small explosion.

- Heat small pieces of selenium together with aluminum powder in a porcelain crucible. The reaction is very vigorous. Sparks are produced, and aluminum selenide (Al_2Se_3) is formed. The heat evolved is sufficient to damage the crucible. If water is added after cooling, highly toxic hydrogen selenide is produced. This experiment must therefore be carried out outdoors with your back to the wind.
Once prepared, the aluminum selenide may be placed in a test tube into which a little water is introduced before sealing it with a stopper fitted with a fine outlet tube. The hydrogen selenide can then be ignited. It burns with a blue flame.
This gas also behaves somewhat like hydrogen sulfide by blackening paper impregnated with lead acetate.
If the crucible has not been too badly damaged, it may be partially cleaned with concentrated hydrochloric acid. This must again be done only outdoors because the gas evolved is highly toxic and attacks the tissues of the mouth and nose.
NOTE: If an excess of selenium was present during the initial reaction, toxic selenium dioxide may also have been evolved.

Phosphorus

Three methods may be used to prepare calcium phosphide...
- Heat very small fragments or powder of quicklime in a porcelain dish. When the material becomes red-hot, carefully project yellow phosphorus or red phosphorus onto it (yellow phosphorus generally gives much better results). A flame and dense white fumes are produced, which should not be inhaled. After the dish has cooled, cover the material with a shallow layer of water. Bubbles are evolved and, as they burst in the air, they produce small white clouds. These are caused by spontaneously flammable phosphine.
- Place a homogeneous 1:1 mixture of powdered quicklime and powdered red phosphorus in a small porcelain crucible 4 cm high and 25 mm in diameter. The mixture must not exceed a depth of 1 cm in the crucible. Heat it with a torch, outdoors and well away from nearby buildings. A flame appears and dense smoke is evolved. Wait until the flame has gone out and allow the crucible to cool slightly before transferring the product to a small, tightly sealed colorless glass bottle. After complete cooling, cover the gray powder with a little water. Small crackling sounds

are gradually heard, accompanied by a garlic odor. These are due to bubbles of phosphine that ignite spontaneously as they burst in the air.

- Introduce a few pieces of well-dried yellow phosphorus into a vertically clamped borosilicate 3.3 glass test tube and quickly cover them, without packing, with several centimeters of freshly prepared powdered quicklime. Using one or two gas burners, heat the tube uniformly from top to bottom until it becomes red-hot as evenly as possible, but without allowing it to soften excessively. When the phosphorus finally melts and vaporizes under the effect of the heat descending from above, it comes into contact with the lime and forms reddish-brown calcium phosphide. Allow the tube to cool, then break it. The phosphide is easily recovered because it separates readily from the unreacted lime. Placed in water, it immediately produces spontaneously flammable phosphine. The experiment also works with slaked lime or red phosphorus, but much less satisfactorily.

- Grind a piece of chromium trioxide about one-quarter of a square centimeter in size to a powder in a small porcelain dish and transfer it to a micro test tube. Add one lancet-tip measure of powdered red phosphorus. Rotate the tube gently to mix the two components thoroughly, then heat it while standing well back. A flame suddenly appears, and the tube remains red-hot for a short time (Illustration 181). After the tube has cooled (it cannot be reused), green chromium(III) oxide (Cr_2O_3), readily recognized by its color, is found among the products (Figure 190).

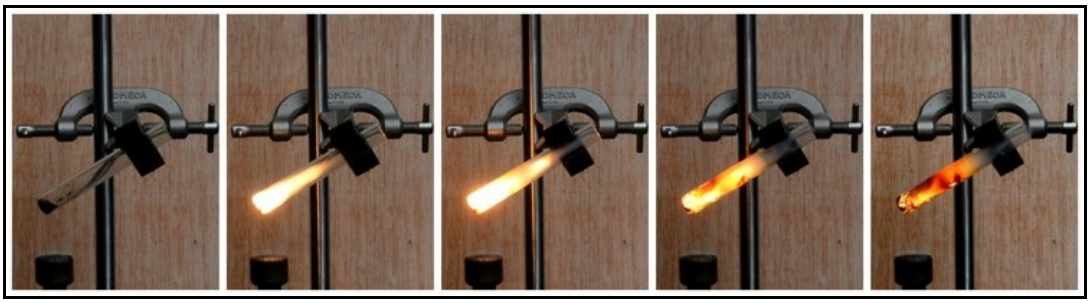


Figure 190

Figure 191

The same experiment may be carried out with yellow phosphorus, using only a piece about the size of half a split pea. The phosphorus melts and then reacts vigorously with the chromium trioxide, producing flame and fumes. After cooling, the walls of the test tube are found to be coated with a red layer. If the tube is filled with water, the liquid slowly becomes green owing to the Brownian motion of fine particles of green chromium oxide. If the water is then poured away and a few drops of nitric acid are added, vigorous effervescence accompanied by reddish-brown fumes occurs because the red layer coating the tube consisted of red phosphorus.
In both cases, the test tube cannot be recovered because part of the chromium oxide has fused with the glass as a result of the intense heat (Figure 191).

- Melt lead in a small crucible. Drop in a small piece of phosphorus. Lead phosphide is formed.

- Place one lancet-tip measure of lead dioxide (PbO_2) together with one lancet-tip measure of powdered red phosphorus in a micro test tube. Rotate the tube gently to mix the two components, then heat while standing at a safe distance. Suddenly, an intensely bright white flame appears together with projections. The reaction, which lasts only a fraction of a second, is explosive in nature, as shown in the accompanying photographs (Figure 192). The bottom of the tube may even burst apart.

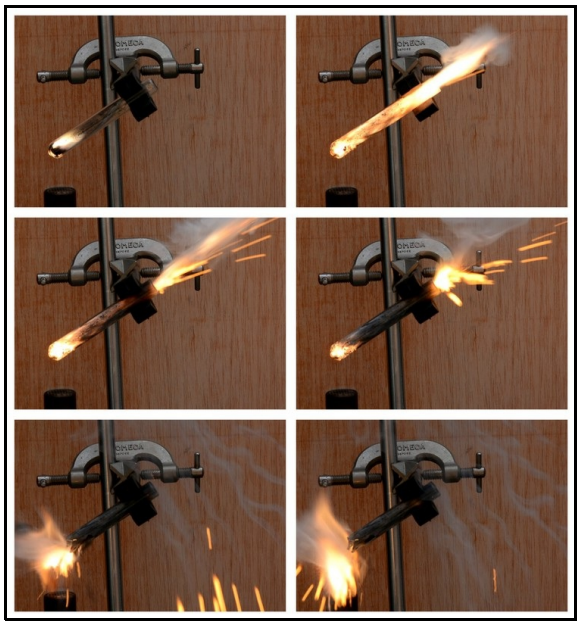


Figure 192

Figure 193

- Fill an ordinary test tube with ammonium nitrate to a depth of a little more than 1 cm and melt it carefully by gradual heating. When the salt has become liquid, drop a small piece of yellow phosphorus into the vertically held tube. A large flame appears, generally rising above the mouth of the tube. Dense white fumes are evolved (Figure 193). Phosphoric acid has been formed.

- Place a pea-sized mixture of red phosphorus and manganese dioxide in a small test tube and heat it. Suddenly, a flame appears and the walls of the tube become coated with yellow and red deposits. Allow the tube to cool, then add one drop of water. A gas appears to be evolved, and the tube fills with white vapor.

- Prepare an intimate mixture of 3 parts flowers of sulfur and 4 parts red phosphorus in a small crucible. Heat the mixture. It ignites, producing abundant white fumes. Once the reaction has ceased, allow the mass to cool. The resulting solid consists of phosphorus sesquisulfide (P_4S_3), which is used in the manufacture of so-called Swedish matches. It is stable and dissolves in carbon disulfide, which may also be used to clean the crucible.

- Place red phosphorus and, a little farther along, magnesium in a silica tube. Pass carbon dioxide through the tube, then heat first the magnesium and afterward the phosphorus. A flame and abundant smoke appear at the end of the tube. Magnesium phosphide has been formed.

- Place one lancet-tip measure of potassium chlorate together with one lancet-tip measure of red phosphorus in a small test tube. The two substances must never be compressed or mixed by shaking. Clamp the tube in place and approach it with a torch. The reaction is almost instantaneous: a large flame and very bright projections burst from the tube with a sharp report (Figure 194).

Figure 194

Another way to proceed is to mix the potassium chlorate and red phosphorus, moisten the mixture, and then heat it very gradually. Soon, sparks are produced, and only a red mass remains. This may subsequently be treated cautiously with nitric acid (the vigorous reaction does not occur immediately).

16.2 Various Mineral Acids and Salts

With Mineral Acids

- Sulfamic acid (also called sulfamidic acid or aminosulfonic acid), commonly used as a descaling agent for household appliances, can be used to obtain sulfur trioxide (SO_3) simply by heating it. To do this, assemble an apparatus fairly similar to that used for an ordinary distillation, taking care to use only wide glass tubes and a well-cooled receiving flask. Heat a small quantity of the acid slowly. White fumes are evolved and a black residue remains. When the receiving flask is opened, a plume

of white smoke escapes. If a few drops of water are allowed to fall into the flask, a vigorous, highly exothermic reaction takes place, accompanied by a hissing sound or a dull explosion. Sulfur trioxide is indeed extremely hygroscopic and reacts readily with water to form H_2SO_4. This can easily be verified by using a pH indicator and then adding a little barium chloride solution to the tube, which produces a white precipitate.
SO_3 can also be prepared in antother way : Heat sodium hydrogen sulfate or potassium hydrogen sulfate. At first, at about 200°C, a pyrosulfate ($Na_2S_2O_7$) is formed. At about 500°C, it is converted into sodium sulfate (Na_2SO_4) and SO_3. The SO_3 is evolved as fairly dense white fumes that may be collected as a solid in a well-cooled flask. As the temperature continues to rise, there comes a point at which the white fumes cease to be evolved. Only molten sodium sulfate then remains in the test tube. Upon cooling, it solidifies and subsequently dissolves readily in water.
NOTE: These reactions are, however, merely a laboratory curiosity. The amount of SO_3 produced is far from substantial, and it would be unrealistic to consider using these methods for the preparation of fuming sulfuric acid which can only be obtained by industrial means.

- In a crucible, heat boric acid. It gradually melts while bubbling, causing the material to swell. If this soft mass is worked with a glass stirring rod, threads can be drawn from it as though it were molten glass. Boron oxide (B_2O_3) is formed.
CAUTION: The crucible is generally ruined. The glass rod is also attacked.

- In a borosilicate glass test tube, heat equal parts of boric acid and vanadium pentoxide. At first, water vapor is evolved. Then, little by little, both substances liquefy and begin to swell into a kind of red magma. Heating must be stopped before the color turns black. Allow the tube to cool, add a little water, and shake. An opaque yellow or greenish liquid is obtained. After standing for several hours, however, the mixture eventually settles by decantation.

With Sodium, Potassium, Ammonium, and Calcium Salts

- Melt a small quantity of sodium nitrate in a crucible, then add a small amount of ammonium chloride. Dense white fumes are produced and, sometimes, flames appear.

- Place sodium bicarbonate in a large test tube connected by a tube to a stemmed glass containing barium hydroxide solution, then heat it. The barium hydroxide solution rapidly becomes cloudy. The bicarbonate has in fact been converted into carbonate with the evolution of CO_2. If heating is continued, a second evolution of CO_2 occurs, this time accompanied by water. The transformation is now proceeding toward the oxide.

- In a test tube, mix powdered black copper oxide with powdered sodium formate. Heat until the mixture melts, then continue heating more gently for a few seconds.

The test tube gradually acquires a brownish coloration. Allow it to cool, then add water. The reddish color taken on by the water shows that copper has been liberated.

- In a porcelain crucible, melt 1 part of KI with 1 part of potassium chlorate. The mixture becomes spongy. Allow it to cool, then dissolve it in hot water. Potassium iodate is thus obtained. It may become yellowish if exposed to light. If a solution of H_2SO_4 is added, all of the I_2 is liberated.

- Place a mixture of KI and magnesium sulfate in a porcelain crucible. Calcine it in air (without a lid). Before long, the white powder turns brown and iodine is liberated.

- In a crucible, gradually melt potassium nitrate. As soon as it has melted, sprinkle it with powdered carbon. Flames and smoke immediately appear.

- In a refractory crucible, heat potassium ferrocyanide in the absence of air. It melts and turns black. Continue heating for quite some time. The constituents separate. N_2 is evolved, while carbon and iron form the black portion consisting of iron carbide. Potassium cyanide also remains and can be recovered by dissolving it in water. It is tested with picric acid, which rapidly turns red.
CAUTION: The crucible is ruined. Some authors recommend carrying out this experiment by mixing 8 parts of ferrocyanide with 3 parts of potassium carbonate, but the result is not different from that obtained with the method described here.

- In a miniature test tube (which will have to be sacrificed), heat a mixture of black copper oxide and sodium cyanide. Very quickly, the mixture appears to boil, and the original gray mass forms a brick-red coating on the walls of the tube. Sodium cyanate and copper have been formed. This can easily be verified by adding a few drops of nitric acid to the tube, which produce reddish-brown fumes and a green solution.

- In a small test tube with an inside diameter of no more than 6 to 8 mm, place at most 1 cm^3 of a mixture of potassium nitrate and sodium acetate. Heat it with a blowtorch while keeping at a safe distance. The mixture first liquefies, then gradually changes in appearance until it reaches a temperature of approximately 350 °C. At that point, the entire mass explodes, violently ejecting a jet of gas from the test tube.

- In a porcelain crucible, heat sodium or potassium cyanide until it melts. When the liquid has become perfectly clear, add lead oxide while stirring with a glass rod for less than one minute. Finally, pour the hot liquid in a long ribbon onto a refractory brick. A bright metallic lead button is obtained. It need only be immersed in water to remove the surrounding salt.
The same experiment can be carried out with antimony or tin oxides.

- In a miniature test tube, mix 1 part of sodium acetate with 1 part of sodium nitrite.

Mix by rotating the test tube, then heat it. Suddenly, a flame and a cloud of smoke burst forth. It is advisable to work only with a very small quantity of material, such as two lancet-tipfuls (Figure 195).

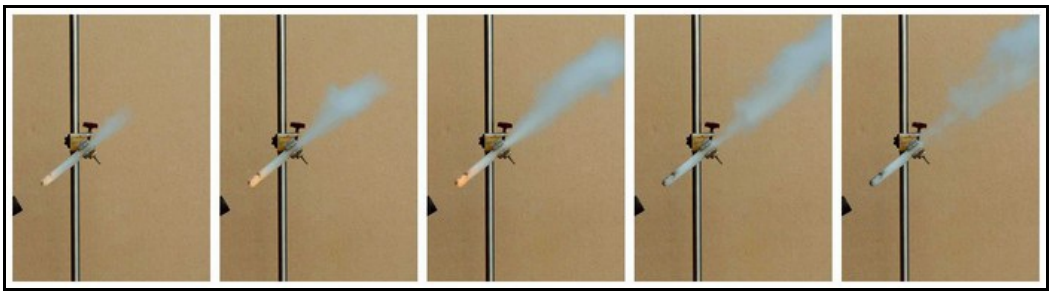


Figure 195

- In an ordinary test tube, place a pea-sized quantity of sodium nitrate and mix it with an equal quantity of sodium acetate. Heat over a flame that is not too strong. The mixture first liquefies and then, at a fairly high temperature, explodes, suddenly propelling a white cloud out of the test tube (Figure 196). Take the usual precautions!

Figure 196

- In a crucible, heat an intimate mixture of 2 parts of potassium sulfate and 1 part of animal charcoal or very finely powdered wood charcoal to red heat for a full five minutes. The black lumps subsequently obtained consist of potassium sulfide, which is readily identified by the gas they evolve when placed in Hcl.

- In a crucible, place 1 part of ammonium chloride with 4 parts of litharge and heat to red heat. After cooling, a yellow substance is obtained. It is the old Cassel yellow once used by painters. It is a mixture, in varying proportions, of lead oxide and lead chloride.

- In a boro 3.3 glass test tube, heat 1 part of ammonium chloride with 1 part of black copper(II) oxide. As soon as fumes begin to escape, both the odor and a moistened indicator paper show that they consist of NH_3. Blue and green colored traces may appear on the inner wall of the test tube. As soon as the contents of the test tube have become black, allow it to cool, then add 5 cm^3 of distilled water. The water turns blue because copper chloride has been formed.
NOTE: The presence of ammonia may produce a precipitate of copper hydroxide when the water is added. A few drops of HCl immediately dissolve this precipitate and restore a green solution.
The same type of experiment can be carried out with other oxides, such as those of lead or zinc, but the result is less demonstrative because the chlorides of these metals are colorless.

- In a crucible, heat a few fragments of quicklime to ensure that all the water originally present has been eliminated and that the substance is indeed CaO. Then transfer the fragments to a glass or porcelain evaporating dish and allow a few drops of water to fall onto them. A hissing sound is heard, and the fragments swell slightly while cracking. If more water is added, the fragments continue to crumble. The lime is said to slake, and the product is therefore sometimes referred to as slaked lime instead of calcium hydroxide.
It is also possible to heat marble ($CaCO_3$) with a powerful Meker burner until the stone is converted into CaO, although the operation is difficult. Using a Meker burner together with a butane/propane torch appears to give better results. This experiment provides a good illustration of the principle used in the lime industry.

- In a long test tube, place an intimate mixture of calcium carbonate and ammonium chloride. Heat the mixture. Ammoniacal water vapor is evolved, recognizable by both its odor and its pH, together with ammonium carbonate, which condenses in the cooler part of the test tube.

With Iron, Zinc, Copper, Nickel, and Lead Salts

- In a test tube, place 1 cm^3 of powdered methenamine mixed with the same quantity of ferric chloride. Add three or four drops of water and heat. A complex is formed, and a strong formaldehyde odor is released.

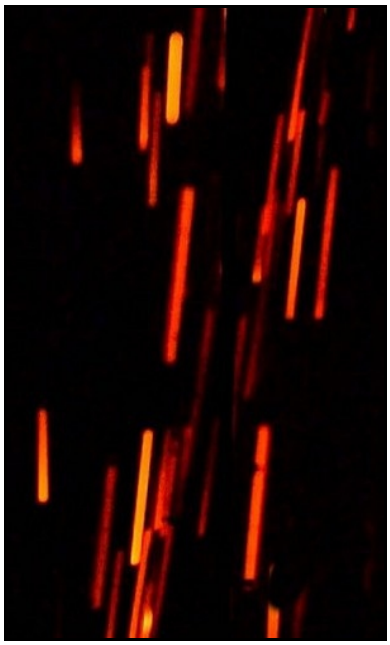


Figure 197

- In a test tube, heat iron(II) oxalate. The yellow powder rapidly turns black and forms a cloud of extremely fine particles before settling again in the tube. Simply invert the test tube at a height of about 1.5 meters (5 ft) above the floor to produce a shower of red sparks somewhat resembling those generated when an iron bar is cut with an angle grinder. Pyrophoric iron oxide has in fact been produced, that is, an oxide capable of igniting spontaneously on contact with air. The experiment is, of course, much more spectacular in the dark or under very dim light (Figure 197).
If iron(II) oxalate is not available, it can easily be prepared by heating a mixture of an oxalic acid solution and a ferrous sulfate solution. A yellow precipitate forms fairly rapidly and can be collected by filtration. It may then be dried and converted into pyrophoric iron oxide by strongly heating.

- In a crucible, heat a small quantity of zinc oxide with four times its weight of powdered carbon to red heat for ten minutes. Small globules of zinc are obtained.

- Prepare an intimate mixture of starch and CuO by grinding them together in a mortar. Then heat the mixture in a boro 3.3 test tube. CO_2 is evolved, and a ring of red copper forms inside the test tube.

- In a medium-sized test tube made of Boro 3.3 glass, place a mixture of black copper oxide and powdered wood charcoal. Heat very strongly while passing the gas evolved through limewater. A white precipitate forms, indicating the evolution of CO_2. The powder inside the test tube turns red and, in some areas, shows the metallic luster of the copper that has formed (Figure 198). The test tube, often deformed by the intense heating, is generally ruined.

Figure 198

- Heat a small quantity of powdered nickel carbonate in a boro 3.3 test tube. The powder turns completely black. Allow it to cool, then add HCl. A beautiful transparent green solution is obtained immediately because both the oxide and the carbonate react with hydrochloric acid.

- Mix 30 g of litharge intimately with 4 or 5 g of finely powdered charcoal, then heat the mixture to red heat in a covered crucible. Metallic lead is formed while CO and CO_2 are evolved.

With Magnesium Salts

- In a porcelain crucible, heat hydrated magnesium chloride. It first becomes liquid, then gradually swells and turns into a white, solid, very light material. HCl is evolved at first, after which the substance is converted into $Mg(OH)_2$ and finally into MgO. The evolution of HCl can easily be demonstrated by bringing near the crucible a flask containing ammonia. White fumes immediately appear. If a little water is poured onto the MgO, highly alkaline $Mg(OH)_2$ is immediately formed.

- In a boro 3.3 test tube, heat magnesium carbonate to 300°C. The gas evolved reacts with limewater because it is CO_2. MgO remains.

- In a test tube, heat a solid mixture of magnesium chloride and manganese dioxide. Chlorine is evolved.

- In a test tube, heat a solid mixture of potassium permanganate and magnesium chloride. Chlorine is evolved.

- In a test tube, heat a solid mixture of magnesium sulfate, sodium chloride, and manganese dioxide. Chlorine is evolved.

With Manganese Salts

- If black manganese dioxide is heated above 1000°C in an open alumina crucible using a Meker burner, the black oxide is converted into red manganese oxide (Mn_3O_4).

- Heat potassium permanganate in a test tube. Oxygen is evolved, and a residue consisting of a mixture of manganate and manganese oxide remains. Dilute it with water and filter. The green color of the manganate appears, while a black insoluble deposit remains.

- In a test tube, slowly and carefully heat a small quantity of potassium chlorate until it has completely melted. Then add a small amount of MnO_2. The characteristic color of potassium permanganate appears. If too much MnO_2 had been added, the mixture would have become black and the color would have been masked.

- In a crucible, heat 1 part of MnO_2 with 2 parts of potassium nitrate. After cooling, dilute the melt with water. A green solution of potassium manganate is obtained. When exposed to air, it gradually turns pink and then violet as potassium permanganate is formed.

- In a porcelain crucible, heat to red heat a thoroughly mixed combination of NH_4Cl and MnO_2. NH_3 and H_2O are evolved and can easily be identified. When the evolution has ceased or greatly diminished, allow the crucible to cool, then dilute the contents with water and filter. Reaction with either a NaOH solution or a potassium ferrocyanide solution shows that manganese chloride has been formed.

- In a porcelain crucible, heat 2 parts of $MgCl_2$ with 1 part of MnO_2. Chlorine is evolved, and manganese chloride is formed. In solution, it can be identified by the precipitates it produces with NaOH or potassium ferrocyanide solutions.

- In a test tube, place an intimate mixture of oxalic acid and manganese dioxide. Heat the mixture and collect the evolved gas in limewater. The limewater rapidly turns cloudy because of the evolution of CO_2. Water and manganese oxalate have been formed in the test tube.

- Heat a small quantity of powdered manganese carbonate in a boro 3.3 test tube. It turns black. Pour a little HCl over it. A very abundant foam is immediately produced, and the odor of chlorine is perceptible. The liquid itself is rather brown in color

With Chromium Salts

- In a test tube, place 1 cm^3 of powdered iron(III) chloride mixed with a small quantity of chromium trioxide. Heat the mixture. Very quickly, the entire mass becomes liquid and turns blood red. An indicator paper inserted at the top of the test tube, where a slight mist is present, shows a fairly high degree of acidity. Among the products formed are blood-red chromyl chloride and hydrochloric acid.

- Carefully melt about 1 cm^3 of potassium chlorate in a test tube, then add a small amount of green chromium(III) oxide. A yellow potassium chromate is immediately formed. When poured into a lead acetate solution, it produces the characteristic lemon-yellow precipitate.
The reaction appears to be improved by mixing the chromium(III) oxide and potassium chlorate with caustic potash.

- In a clay crucible, melt a mixture of solid NaOH and green chromium oxide using a Meker burner. The hydroxide first liquefies and soon forms a dark green liquid. By stirring with a glass rod, the entire mass can be gathered into a solid lump that retains the same color. Continue heating to red heat. Little by little, the color changes and becomes olive green, while the substance once again becomes pasty. Allow it to cool, dilute with distilled water, and let it settle for 24 hours to obtain a beautiful yellow liquid. Its reaction with lead acetate, producing a yellow precipitate, indicates that the solution consists largely of potassium chromate.

- In a crucible, heat green chromium oxide with sodium carbonate and sodium nitrate to red heat. Once the mixture has become liquid, continue heating for a short time, then allow it to cool. Finally, dilute with water and allow it to settle. The yellow supernatant solution contains potassium chromate, recognizable by the yellow precipitate it produces with a lead acetate solution.

- The following experiment is somewhat unusual because it requires no external heating. Place a small pile of potassium dichromate in a porcelain crucible and completely wet it with alcohol, which is then ignited. Chromium oxide is formed.

- In a crucible, heat 100 g of boric acid with 33 g of potassium dichromate. The mixture melts and gradually forms a kind of red vitreous paste from which threads can be drawn when stirred with a glass rod. Allow it to cool, then mix it with water. The orange-yellow potassium chromate dissolves, leaving an insoluble green chromium hydroxide known to painters as Guignet green.

- In a crucible, heat solid potassium dichromate with flowers of sulfur. Once the

mixture has melted, stir it with a glass rod. Small sparks may be produced. After cooling, add water. The characteristic yellow color of a chromate is readily recognized.

With Antimony and Arsenic Salts

- Mix tartar emetic (potassium antimony tartrate) with charcoal and heat the mixture to red heat in a covered porcelain crucible. Allow it to cool. Upon opening the crucible, a kind of crust is observed on the surface of the solid. If the material is stirred with a glass rod, a few tiny flames or glowing spots become visible. When poured into water, the solid produces a strongly alkaline pH, unlike an ordinary solution of tartar emetic. Some books state that the substance has become pyrophoric and may ignite, sometimes even with detonation, if projected into moist air. Apart from the small flames mentioned above, I have not observed any other pyrophoric properties.

- Hold a boro 3.3 tube vertically with a clamp. Place a small quantity of potassium nitrate in it and heat until it melts. Then add some powdered antimony sulfide (Sb_2S_3). The combustion is vigorous and produces a considerable amount of yellow fumes (Figure 199).

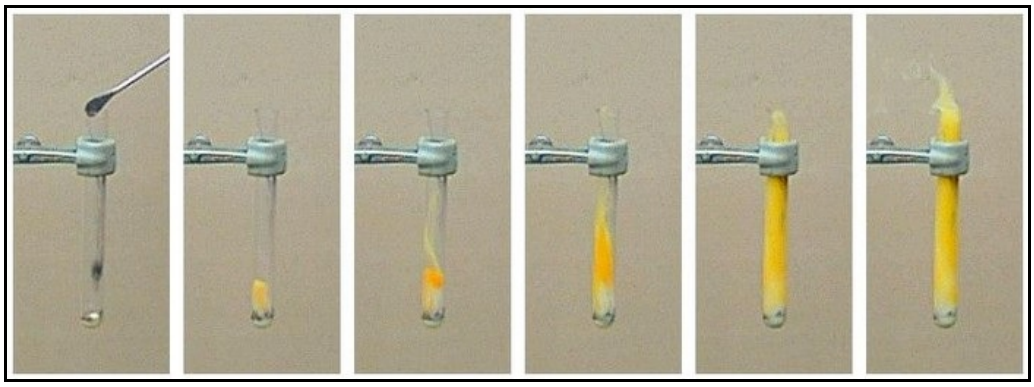


Figure 199

- In a long test tube, heat an intimate mixture of finely powdered charcoal and arsenious oxide. Slightly above the heated zone, a mirror-like ring forms on the inner wall of the test tube. It consists of pure arsenic.
In this experiment, arsenious oxide may be replaced by various arsenic salts.

- In a long test tube, heat a small quantity of orpiment (an arsenic sulfide mineral). The sulfur is driven off and condenses in the upper part of the test tube, while a globule of pure arsenic is formed. It can easily be detached from the cooled test tube. This is a simple method for preparing metallic arsenic and closely resembles that used to prepare metallic mercury.
This metallic arsenic should not be confused with the powdered poison that many novelists refer to by that name, which is in fact arsenious oxide.

Vanadium Salts and Vanadates

- In a small porcelain crucible, prepare an intimate mixture of vanadium pentoxide and lithium carbonate. Heat the crucible to red heat until its contents become white. Allow it to cool, then add water to dissolve whatever will dissolve. Add a few drops of acetic acid to the resulting white suspension. An orange-yellow color is obtained. If two or three drops of the same acid are added directly into the crucible, a distinctly redder liquid is produced. The same acid added to a colorless (very dilute) aqueous solution of vanadium pentoxide or lithium carbonate produces no coloration. In fact, lithium vanadate has been formed, which reacts with the acid to produce a color ranging from yellow-orange to red, depending on the concentration.

With Salts of Other Metals

- To a solution of mercury(II) chloride or mercury(II) nitrate, add an excess of a sodium hydroxide solution. Wash the resulting yellow precipitate thoroughly, then dry it with a heat gun or a hair dryer held at a reasonable distance. Place a portion of the resulting yellow powder in a micro test tube, then mix it with one-fifth its weight of powdered sulfur. Heat gently. Suddenly, decomposition occurs, accompanied by the release of a dark cloud. Sometimes, the abrupt evolution of this cloud, consisting of mercury sulfide, is accompanied by a small explosion. This mixture is known as Bayen fulminating mixture (Figure 200).

Figure 200

- In a crucible, place a small quantity of cobalt chloride, the same quantity of flowers of sulfur, and twice that quantity of powdered sugar. Mix the three components thoroughly, then heat them. The mixture melts, turns black, and swells considerably (use a sufficiently large crucible). In the end, only a very light solid resembling a large meringue remains. The crucible is generally ruined.

- Heat a spatula-tip quantity of neutral cobalt(II) carbonate ($CoCO_3$) in a boro 3.3 test tube. The pink powder suddenly turns black. Allow it to cool, then pour concentrated HCl over it. A beautiful blue solution is immediately obtained, although not all of the black powder dissolves. Complete dissolution requires several days, and a generous quantity of acid should be used.

- Add a NaOH solution to a solution of mercury(II) chloride. A beautiful yellow

precipitate immediately forms. Allow it to settle, then dry it. Mercury(II) oxide has thus been obtained. When mixed with ammonia, this precipitate forms a yellowish-white complex that dissolves in HNO_3. When heated, it becomes increasingly red until it reaches a brick-red color. If heated still further, it releases oxygen (which relights a glowing splint) and mercury. Mixed with sulfur and then heated in a porcelain dish, it forms a sulfide that decomposes completely on heating, releasing mercury vapor and sulfur dioxide. This entire series of manipulations must be carried out outdoors because of the highly toxic mercury vapors.

- Pass a stream of H_2S over an open crucible, heated in the open air and containing a mixture of barium hydroxide and NaOH. Incandescence occurs.

- In a miniature test tube, mix equal parts of powdered carbon and barium peroxide. Heat the mixture. Sparks are produced, and barium carbonate is formed.

- Place a few pieces of alum stone in a crucible. As heating proceeds, the translucent material becomes opaque white while increasing in volume, often overflowing the crucible in the form of a kind of mushroom. Anhydrous alum has thus been obtained.

- In a borosilicate glass test tube that will have to be sacrificed, heat together sodium hydrogen sulfate and titanium dioxide. The mixture melts rapidly, then white vapors are evolved. The mass solidifies again while gradually becoming yellow, a color that disappears upon cooling.

- Heat molybdenum(VI) oxide in a boro 3.3 tube. The grayish-blue powder turns lemon yellow. Upon cooling, it becomes gray again.

16.3 Various Organic Substances

- Place a very small quantity of picric acid (one spatula tip) in an ordinary test tube. Heat it while taking great care to keep the tube well away from yourself and with its opening directed away from your face. Suddenly, a flame appears accompanied by an explosive report. This demonstrates that picric acid is a powerful explosive.

- Arrange a sacrificial test tube horizontally or with only a slight inclination and fill it loosely with sawdust. Using a cork stopper fitted with a short glass tube, connect this test tube to a small flask placed in a freezing mixture (ice + $CaCl_2$). The flask is fitted with a delivery tube ending in a fine jet. Heat the test tube. Various substances are evolved, some of which condense in the small flask. Among them are tar and water. A gas issuing from the jet may be ignited. The same experiment may be carried out with bituminous coal, which generally produces even more gas. The small flask can easily be cleaned with ether, whereas cleaning the test tube is not worthwhile. The production of this flammable gas explains the rapid spread of forest fires.

- Place a mixture consisting of two parts potassium chlorate and one part manganese dioxide in a fairly wide test tube clamped vertically to a stand outdoors. For safety reasons, the mixture must not occupy a volume larger than that of an olive. Heat it with a portable Bunsen burner until it melts and oxygen bubbles begin to appear. Immediately remove the burner and drop in a pea-sized lump of sugar. A large flame appears together with abundant fumes. The heat evolved is intense.

- Place a mixture of 9 g of powdered quicklime, 6 g of powdered potassium hydroxide (or sodium hydroxide), and 6 g of powdered sodium acetate in a sacrificial test tube 3 cm in diameter. Close the tube with a stopper fitted with a fine outlet tube. Heat until much of the mixture melts and reacts with the remainder. When you are certain that the evolving gas has completely displaced the air from the tube, ignite it at the end of the outlet tube. The gas is methane. The potassium hydroxide attacks the glass, which is why the test tube is sacrificed. The experiment may also be carried out without quicklime, which merely serves to reduce the attack of potassium hydroxide on the glass.
CAUTION: Before igniting the gas, be absolutely certain that all the air has been expelled from the test tube; otherwise, an explosion will occur (the type of firedamp explosion once encountered in coal mines).

- Heat sodium formate in an ordinary test tube closed with a stopper fitted with a fine glass outlet tube. When the sodium formate has melted, bring the end of the outlet tube into contact with a flame. Ignition occurs. If heating is continued, the flame changes in appearance. This is because hydrogen is evolved at first, followed later by carbon monoxide. The outlet tube must therefore not be brought to the flame too soon, otherwise the test tube may burst because of the explosive hydrogen-air mixture (Figure 201).

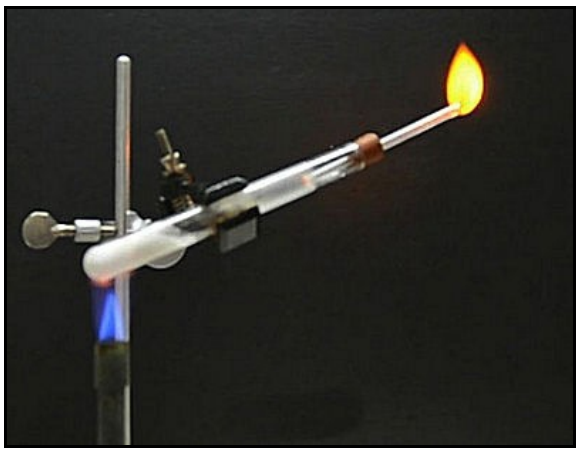


Figure 201

If, instead of heating sodium formate alone, a mixture of sodium formate and sodium hydroxide is heated, only hydrogen is evolved, and it may be ignited. The hydrogen flame, normally pale blue, appears yellow because of the presence of sodium ions. Sodium carbonate remains in the test tube and, after cooling, reacts vigorously with a few drops of hydrochloric acid to produce readily identifiable carbon dioxide.

- Place, successively, one teaspoonful of phenol, one teaspoonful of potassium hydroxide, and finally one teaspoonful of slaked lime into a crucible. Heat while stirring with a glass rod. A first partial liquefaction occurs, followed by solidification, and then by complete liquefaction. Finally, the liquid gradually changes from yellow to green and then to purplish-red. Rosolic acid has been formed. Continued heating results in carbonization.

- Heat a mixture of glucose and phosphorus pentoxide in a large test tube. Slight warming immediately produces carbonization.

- Heat a mixture of urea and soda lime in a large test tube. Direct the evolved gas toward a strip of moist pH paper positioned just above a small bottle containing hydrochloric acid. The alkaline pH and the white fumes of ammonium chloride indicate that ammonia is being evolved.
Heat urea slowly in a large test tube. It first melts to form a transparent liquid and then gradually evolves ammonia and water vapor. The liquid suddenly becomes milky and then white, resembling limewater. Continue heating until only a solid remains. Near the mouth of the tube, urea is seen to reform through the combination of ammonia with a small amount of cyanic acid. Allow the tube to cool, then gradually add concentrated sulfuric acid. Crush the white solid in the acid with a glass rod and heat again until a transparent, possibly slightly yellow, liquid is obtained. Allow it to cool once more, then add concentrated nitric acid drop by drop. The contents of the tube become hot and foam vigorously while abundant vapors are evolved. When the addition of nitric acid no longer produces foaming, allow the now white liquid to cool slightly and then gradually add water. Cyanuric acid precipitates.
NOTE: Cyanuric acid is more easily prepared by passing a stream of chlorine over molten urea in a tube.

- Heat urea in a test tube until it melts. An odor of ammonia becomes noticeable. Continue heating for only a few more seconds, then cool the tube under running cold water. Add water followed by a few drops of sodium hydroxide solution. Dissolution is difficult, but once it is clearly underway, add one drop of copper sulfate solution. The solution immediately turns red-violet. This is known as the biuret reaction.
A variation of this experiment also exists. Heat the urea well beyond its melting point until only a white solid remains. Dissolve this solid in water, crushing it if necessary with a thick solid glass stirring rod. Then add only a very small amount of sodium hydroxide solution. The milky liquid becomes completely clear. Finally, add a few drops of copper sulfate solution and shake vigorously. The copper hydroxide precipitate that first appears rapidly disappears, and the entire liquid turns mauve to violet, depending on the concentrations.

- Heat urea nitrate in a test tube. At about 140 °C, nitrogen, carbon dioxide, and nitric oxide are suddenly evolved. If heating is continued, additional gases are evolved, namely nitric oxide, carbon dioxide, and ammonia.

- Heat a mixture of crystalline citric acid and manganese dioxide in a large test tube. Pass the evolved vapors first through a cooled tube and then into a flask containing limewater. The limewater rapidly turns milky. The liquid collected in the cooled tube is acetic acid. Other substances are also evolved, as indicated by an odor of burnt wood. Two pyrolysis acids remain in the test tube: citraconic acid and itaconic acid.

Chapter 17 - Electrochemistry and Physics Experiments

17.1 Electrochemistry

Some people will say that electrolysis experiments are among the simplest to perform because they require very little equipment. This is both true and false. Professional electrodes are extremely expensive and can only be purchased from specialized suppliers. There are nevertheless various ways of constructing inexpensive and highly effective equipment.

The simplest approach is to work with a U-tube in whose branches the electrodes can easily be mounted. These may simply consist of metal sheets connected directly to alligator clips attached to the electrical power source. Of course, such electrodes may also be placed in an ordinary beaker, but it is sometimes less easy than in a U-tube to observe what is happening at each electrode.

The electrical power source may consist of a battery or of an adjustable DC power supply such as those found in electronics laboratories or even in the low-current power supplies of certain electronic devices.

If one wishes to collect and identify gases produced during electrolysis, a professional voltameter (Hofmann voltameter) should be used, or one can be constructed from several tubes. The basic principle consists of introducing the electrodes from below into interconnected tubes. It is not difficult to manufacture electrodes for a homemade voltameter. Hollow glass tubes are used, through which a wire of steel, copper, or another metal is passed as required. The hollow space inside the tube is then sealed by injecting sanitary-grade silicone. Figure 202 shows two pairs of electrodes (steel and copper) prepared in this manner.

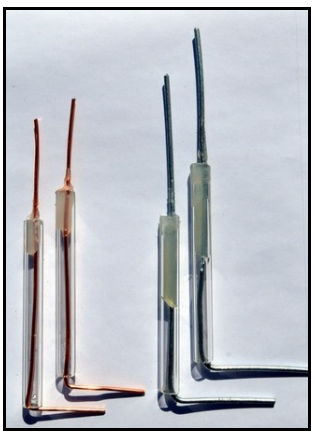


Figure 202

Almost any salt solution imaginable may be subjected to electrolysis, yielding a great variety of results that cannot be discussed here. The following examples are easy to perform and may provide a few ideas. These experiments present virtually no danger other than the risk of electric shock for the careless experimenter. Attention must nevertheless be paid, in certain cases, to the evolution of highly toxic chlorine gas.

Figure 203

- Two tin-wire electrodes are immersed in a hydrochloric solution of tin chloride. As soon as the current is applied, fine tin needles form on one electrode (Figure 203) while apparently nothing happens at the other electrode. If the current is reversed, the fine needles immediately fall away from the electrode on which they had accumulated and others begin to form on the opposite electrode.

- Prepare an aqueous solution of KI and place copper electrodes in it. Hydrogen is evolved at one side while iodine rapidly colors the other side. If the experiment is carried out in a U-tube, a drop of phenolphthalein may be added to the starting solution, producing markedly different colors in the two branches.

- In an aqueous solution of copper sulfate acidified with H_2SO_4 and containing two copper electrodes (or, better still, carbon electrodes), a rapid formation of large deposits is observed as soon as the current is applied. At first sight these deposits appear black, but when collected they are red in color. When placed in slightly diluted nitric acid, they color the liquid blue and are therefore indeed pure electrolytic copper.

- Place two copper electrodes in a saturated aqueous NaCl solution heated to just below its boiling point. The liquid foams strongly and rapidly becomes brick red in color. Allow it to stand. A deposit forms, consisting of cuprous oxide, Cu_2O, which is insoluble in water.

- Take a small quantity of a dilute nickel sulfate solution and add ammonia until a fairly pale blue solution is obtained. Connect a demonetized coin made of nearly pure nickel to the positive electrode (many such coins once existed and are now of little value). Connect a copper strip to the negative electrode. Apply the current only for a short time. The copper then becomes covered with a bright layer of nickel. If the current is allowed to flow for a longer period, a substantial nickel deposit forms and eventually separates from the copper.

- Finally, here is a spectacular variation of the classical electrolysis of salt water. Prepare a solution of table salt (NaCl) and add two drops of phenolphthalein. As soon as the current is applied, a magnificent red-violet coloration appears on one

side of the solution, which was initially colorless. This coloration is due to the formation of sodium which, upon contact with water, is immediately converted into sodium hydroxide, a base that causes the pH indicator to change color. This experiment may of course be performed with other indicators such as bromothymol blue, which will color the starting solution yellow-orange and produce a beautiful blue cloud at one of the electrodes as soon as the current begins to flow. These experiments are naturally more spectacular when presented in a large U-tube.

Electricity can also be involved in another type of experiment in which sparks are used. A famous experiment of this kind demonstrates that two volumes of hydrogen mixed with one volume of oxygen form water when an electric spark is produced within the mixture.

In the past, this experiment was carried out in what was known as an eudiometer, consisting of a very sturdy glass tube whose upper end was fitted with two thin electrodes between which a spark could jump.

Another experiment, perhaps even more spectacular, can be performed using electrical equipment capable of producing a large number of sparks. It is carried out in a flask with three or four necks. Two of the necks are used to insert electrodes positioned facing each other a short distance apart. The other two are used respectively to introduce air and to expel the gaseous contents of the flask into a Drechsel bottle containing a small amount of water.

Initially, the flask should contain only air. After sparks have been produced in it for a prolonged period, the gas acquires an orange color. It is then expelled by introducing fresh air, and the operation is repeated several times. Eventually, the water in the Drechsel bottle is found to contain nitric acid.

The explanation is as follows: nitrogen and oxygen from the air combine under the action of the electric sparks, first forming NO, which is then oxidized to NO_2. When NO_2 comes into contact with water, both nitrous acid (HNO_2) and nitric acid (HNO_3) are initially formed. In the presence of oxygen, the nitrous acid is subsequently oxidized, ultimately resulting in the formation of additional nitric acid.

17.2 Three Physics Experiments

Chemistry and physics are two sciences that often complement one another because the experimental work of the former frequently relies upon elementary concepts from the latter (pressure, communicating vessels, and so forth).

In this respect, here are three experiments that I consider indispensable from an educational point of view.

- Take a narrow tube approximately 100 cm long and fill it with mercury. Then invert it into a small mercury trough. The mercury falls inside the tube until it reaches a height which, relative to the surface of the mercury in the trough, corresponds exactly (in millimeters) to the atmospheric pressure. This is a true mercury barometer and this is the famous experiment first performed by Torricelli.

- Fill a test tube with 3 or 4 cm of glycerin and then immerse it in a small beaker that has also been filled with glycerin. The test tube appears to disappear from view, at least up to the level occupied by the glycerin. It is simply a matter of refractive index...

- Place approximately 400 mL of water in a 1 L flask and bring it to a boil. Stop heating and wait until the boiling subsides. Then close the flask with a rubber stopper and quickly invert it so that the neck points downward. The surface of the water then becomes perfectly calm. Pour a little cold water over the flask. Immediately, boiling resumes for a short time and then ceases again. Pour cold water over it once more and, once again, boiling resumes. And so on, many times. This is a simple way to demonstrate that the boiling point is related to pressure (atmospheric pressure).
Another way to demonstrate the same principle is by means of a desiccator. Place a beaker containing a little water inside the desiccator and close it using the lid fitted with a stopcock outlet. Connect this outlet to a vacuum pump and start the pump. Very quickly, bubbles can be seen rising through the water and the water begins to boil. The stopcock may then be closed, the vacuum created inside the desiccator being sufficient to allow the boiling to continue. If a sufficiently powerful vacuum pump is not available, the water may be warmed slightly before being placed in the desiccator, while ensuring that its temperature remains as far as possible below 100°C. By replacing the beaker of water with a bell, it is possible to demonstrate in the same way that sound does not propagate through a vacuum.

Chapter 18 - Cleaning Laboratory Glassware

Cleaning laboratory glassware is the least pleasant task that either the professional or amateur chemist must perform. It is nevertheless an essential task that requires a certain degree of care.

In a specialized analytical laboratory, it is essential to use glassware that is ultimately rinsed with distilled water. This is by no means necessary, however, in a high-school or amateur laboratory. In most cases, it is sufficient to use an ordinary dishwashing detergent, rinse thoroughly, and immediately dry each bottle or vessel upside down. If one lives in an area where the water is so calcareous or rich in iron that it leaves significant deposits on the glassware, an excellent and economical rinse water can be obtained from rainwater collected in such a way that it remains perfectly clear.

Various bottle brushes should be used, together with a synthetic foam sponge having on one side a non-metallic scouring surface. Glassware should never be cleaned with steel wool. Care should also be taken to ensure that bottle brushes do not have an exposed metal end, since this may cause glassware to break. Sometimes, this problem can be solved simply by bending the end of the brush upward with pliers.

Certain deposits resist cleaning with ordinary detergent and a bottle brush. The following hints may therefore prove useful.

Cleaning a Flask Containing Sulfur Adhering to the Walls

It is useful to keep on hand a solution of ammonium sulfide which, after being converted into yellow polysulfide by contact with air, acquires the ability to dissolve sulfur efficiently. Depending on the amount of sulfur present in the flask, the action may be instantaneous or may require several days. Warm aniline may also be used, but this is a considerably more expensive method.

Cleaning Glassware Coated with Organic Substances

Pour in an alkaline potassium permanganate solution and allow it to act for several hours. Then discard the solution and remove the manganese dioxide that has formed by means of HCl or H_2O_2.

Cleaning a Flask that Has Long Contained Copper Sulfate

Over time, copper sulfate solution deposits a small amount of copper on the walls of the glass flask, giving the glass a dull brownish-green appearance. To restore the flask to its original condition, it is sufficient to wash it with dilute nitric acid.

Cleaning Glass Blackened by Carbonaceous Matter

Heat it with powdered MnO_2, provided there is not too much material to be removed.

Cleaning a Glass Tube to Which Green Chromium Oxide Has Adhered

The green chromium oxide that adheres to glass walls when formed during certain combustion experiments cannot be dissolved by acids. There are, however, two methods for cleaning glassware so contaminated:
- Prepare a mixture of sodium nitrate and potassium carbonate and heat it until fusion occurs on the areas where the oxide has adhered. After cooling, the yellow chromate formed should be removable by simple washing with water.
- Heat a mixture of concentrated nitric acid and a little powdered potassium chlorate. The color of the liquid immediately changes to greenish-yellow owing to the formation of a chromate.

Fragments of Phosphorus Adhering to the Glass Walls of a Flask

It sometimes happens during experiments involving burning phosphorus that orange-yellow stains appear on the glass walls of the flask. These may be removed carefully with dilute nitric acid (beware of possible splashing).

Potassium Permanganate Stains

The smallest grain of potassium permanganate can stain a laboratory bench or sink if the surface is damp. Such stains can easily be removed with hydrogen peroxide or sodium bisulfite.

Restoring a Gold Jewel Stained by Mercury

During experiments involving mercury, it may happen that a droplet of mercury comes into contact with a gold ring or bracelet that the experimenter forgot to remove. It is often said that the jewel is then permanently damaged. Not at all! Simply place it in dilute nitric acid for a few hours and then polish it with a chamois leather.

Miscellaneous Stains

Many different stains resulting from inorganic chemistry experiments can be removed with hydrochloric acid or nitric acid, or even a mixture of both to form aqua regia. This is generally the first method to try. Another fairly effective method is the use of the sulfochromic mixture whose composition was given earlier. Hydrogen peroxide may also be tried, but always with caution.
A particular mixture can also be used to remove various organic deposits adhering to glassware. Pour a quantity of concentrated sulfuric acid into the contaminated vessel. Then add one-third as much hydrogen peroxide. Ratios of one-fourth or one-fifth may also be used, depending on the vigor of the reaction desired. This mixture is known as piranha solution. It is both highly acidic and strongly oxidizing, making it particularly suitable for destroying organic matter. It should never be prepared in advance and stored. Some chemists recommend replacing the acid with a concentrated ammonia solution. The resulting liquid is also highly oxidizing, but this time alkaline.
Other stains, resulting from organic substances, can be removed by various solvents. It is best to begin with the least expensive or least pure grades (which can often be purchased from hardware stores): ethyl acetate, aceton, paint thinners, ether, chloroform... Various alcohols are also effective in certain cases.

Table of Nearly 120 Analytical Experiments

Today, professional laboratories are equipped with specialized reagents and automated instruments that can quickly identify certain substances—or even every component of complex mixtures. However, this was not always the case.

In the past, chemical analysis relied on numerous experimental procedures whose basic principles are still well worth understanding. For example, in order to identify mineral salts, chemists caused them to react in solution with reagents capable of producing precipitates or changes in the color of the liquid. The appearance of the precipitates and their colors alone, by successive comparisons, made it possible to determine some of their constituents.

On the following page, the reader will find a table briefly summarizing the various types of precipitates and color changes that can be obtained by reacting simple reagent solutions at room temperature with various salt solutions.This table alone contains nearly 120 different experiments that can easily be carried out! Amateur chemists will therefore find plenty to satisfy their enthusiasm, while teachers will have an opportunity to present an excellent lesson in which different groups of students can take part as experimenters.

Before proceeding, however, several points should be clarified...

The appearance and color of precipitates often vary depending on the concentrations of the solutions used, as well as on their pH. Chemists therefore often recommend carrying out some of these experiments in slightly acidic or alkaline media in order to obtain more pronounced effects. However, at an elementary level, this precaution can usually be dispensed with. A few unavoidable exceptions must nevertheless be taken into account. For example, tin chloride can only be dissolved in water acidified with hydrochloric acid and, consequently, its reaction with an alkali carbonate initially produces mainly carbon dioxide. In this case, it is therefore necessary to work with a very concentrated carbonate solution, or even by adding the undiluted salt directly to the tin chloride solution.

Furthermore, some salts in their neutral form are not always easy to obtain or dissolve in water. A few practical expedients may then be employed. For example, to obtain an aluminum salt solution, a solution of alum may be used, since the potassium compound does not interfere with the reactions described here.

Finally, the quality of the reagents themselves must also be taken into account. For example, an alkali sulfide may contain significant amounts of polysulfides, which can produce slightly different precipitates.

Precipitates and Color Changes Produced at Room Temperature by Mixing Certain Salts with Specific Reagents

Metal ion	NaOH solution	NH4OH solution	Potassium ferrocyanide	Potassium thiocyanate	Sodium sulfide	Alkaline carbonate	Miscellaneous reactions
Aluminium (III)	white soluble in excess	white insoluble in excess		white	white	white	white with sodium phosphate
Barium (II)	delayed white			white		white	white with diluted H2SO4
Cadmium (II)	white		yellowish-white	white	yellow	white	white with alkaline phosphate
Cobalt (II)	blue -> green in air	blue-green soluble in excess	green	brown	black	pink to red or violet	
Copper (II)	light blue	deep blue soluble in excess	reddish-brown	black	black	light blue	with tannic acide : turns blue-black
Iron (II)	white then yellow-red in air	greenish-white becoming red	greenish-white becoming blue	brown coloration	black	yellowish-white	blue with potassium ferricyanide
Iron (III)	brick red	brick red	blue	blood red coloration	black	brick red	black with tannic acid / S with H2S
Lead (II)	white	white	white	white	black	white	with tannic acide : flocculent white
Magnesium	white	white				white	white with ammonium phosphate
Manganese (II)	pinkish-white then brown with air or H2O2	pinkis- white then brown with air	white	whitish	pinkish-white	white	white with potassium oxalate / colloidal white with tannic acid
Mercury (I)	black	black	gelatinous white		black	black	white with HCL / red with K2Cr2O7
Mercury (II)	yellow	white	white		black	brown	red with KI soluble in excès
Nickel (II)	apple-green soluble in NH4OH	blue	white-yellow or white-green	white forming slowly	black	light green	with tannix acide : flocculent white
Silver (I)	light brown or olive		white	white	black	off-white	white with HCl, darkens in light
Tin (II)	white, soluble in excess	white	white		chocolate brown	white	gray Hg with mercuric chloride / zinc becomes covered with needles
Zinc (II)	white	white	white	colloidal white	white	white	

ADANDONED PLACES

All over the world, there are undoubtedly laboratories and chemical supply warehouses that have been forced out of business. Large quantities of chemicals and equipment are thus left abandoned and may represent a serious source of danger to the unwary—or a source of delight to amateur chemists...

One such place, where the author and his wife spent many hours marveling at their surrundings despite the freezing cold conditions...

ADDENDUM 1

How to Measure Temperatures

At first sight, one might think that measuring a temperature simply requires a thermometer. Certainly; but what type of thermometer, how should it be used, and where should it be placed? Those are the important questions I am going to answer.

The most traditional thermometer used in a chemistry laboratory is cylindrical in shape and contains a liquid that expands or contracts within a capillary tube. Older thermometers contained alcohol or mercury. Today, however, because of regulations governing the use of mercury, the latter is increasingly being replaced by various colored liquids of different compositions. Thermometers are manufactured with temperature scales that vary according to the model. For thermometers of equal length, the wider the scale range (for example, 0 to 400°C rather than 0 to 100°C), the less precise the graduations can be. It is therefore useful to own several thermometers with different ranges. Preference should always be given to thermometers whose graduations are engraved on a plate fixed inside the tube rather than printed on the outside surface, because the latter will gradually wear away through repeated handling and washing.

These thermometers must be placed at the exact location where the temperature is to be measured, either within a liquid or just at the point where vapors enter a condenser. Great care must be taken when inserting such thermometers into a hole drilled through a rubber stopper or when removing them. Indeed, it is during this operation that these delicate instruments are most often broken, sometimes causing serious injuries such as severed tendons in the hand. Before inserting the thermometer, it is useful to lubricate the hole in the stopper with glycerin or even with a special grease normally intended for stopcocks.

There are also electronic thermometers. The simplest consist of a metal probe that can be inserted into a liquid or a solid. The temperature is displayed immediately on an LED-type screen. These thermometers, now commonly found in kitchens, usually operate from a button cell battery. If they must be immersed in a liquid or exposed

to vapors capable of attacking the metal probe, they must be placed inside a glass sleeve into which a little oil has first been introduced. This allows the temperature of the liquid or solid being measured to be transmitted to the metal probe after warming the sleeve. In such cases, the temperature reading may naturally be somewhat delayed. Sleeves designed for these thermometers are available in the form of modified male ground-glass joints or are sometimes incorporated by glassblowers into certain adapters or Vigreux columns (Figure 27 page 39).

Finally, there are thermometers that measure infrared radiation. Advertisements for these instruments claim that they can measure temperature at a distance (without contact), even inside a flask. This is not correct. Such thermometers are indeed capable of taking measurements from a distance, but they record only surface temperatures and not the temperatures inside the objects at which they are aimed. They are therefore suitable for measuring the temperature of a liquid contained in the bulb of a flask because the liquid brings the glass to the same temperature. They are not suitable, however, for measuring the temperature of a reaction occurring in the middle of a liquid or a solid contained within a flask.

ADDENDUM 2

Baumé Degrees

The amateur chemist may occasionally be surprised to discover, in a catalog, on a bottle, or in an old chemistry book, a notation such as "66° Bé." What exactly does this mean?

It was the chemist Antoine Baumé (1728–1804) who invented this system based on the density of liquids in relation to their concentration. Although it was used for a long time, the Baumé degree (generally written "°Bé") was eventually removed from the list of legal French units of measurement in 1961. In other words, if it is still used here and there, it is purely by tradition.

Outside the field of chemistry, the Baumé degree was mainly used in the culinary arts to measure the sugar concentration of syrups. In that field, it has been replaced by the Brix degree.

Calculating the density of a liquid from its Baumé degree is not straightforward. If one encounters an old experimental description using this system, the best solution is still to have access to a suitable densimeter graduated in Baumé degrees.

One of the few chemicals still sold with its Baumé degree indicated is sulfuric acid. It is therefore worth remembering that 65° and 66° Bé correspond respectively to concentrations of 92% and 96%.

ADDENDUM 3

How to Bend Glass Tubing

Specialized suppliers sell a few simple types of glass connecting tubes intended to be inserted into holes drilled in certain stoppers. However, the true laboratory worker should never hesitate to make the tubes that best suit his own needs. In fact, this is not a particularly difficult task.

The tubing to be used must be purchased either from a glassblower or from a specialized supplier. It is preferable to choose borosilicate 3.3 glass tubing because its softening temperature is higher than that of soda glass and it therefore bends less suddenly. At the beginning, tubes having an outside diameter of 8 mm should preferably be selected.

To bend a tube at a right or acute angle, it must be heated over a length of 6 or 7 centimeters by means of a burner or torch fitted with a "butterfly" attachment that produces a thin, elongated flame. The tube is held between the fingertips of both hands, which remain about 30 centimeters apart, and is heated at the point where it is to be bent while being rotated continuously so as to obtain heating and softening that are as uniform as possible.

When the flame, upon contact with the tube, turns orange and the tube itself begins to glow red, it is sufficient to bend it to the desired angle while keeping the outer side of the bend toward the flame. This is because that side must stretch more than the opposite side.

To make a "duckbill" tip, a tube is heated in the same manner, but over a shorter length. When the flame turns orange, the tube is pulled by moving the hands outward. Conversely, to produce small beads or a "nipple" that provides a better connection between a glass tube and flexible tubing, the tube is compressed before the flame even becomes orange. This produces a deformation somewhat resembling an olive. The same operation is then repeated 15 mm farther along and finally once again between the two deformations already obtained. One merely has to ensure that both ends of the tube always remain aligned so that the deformations form an acceptable « hose barb.» It will certainly not be as regular as those produced by professional glassblowers using specialized equipment, but it will be just as effective.

All of these operations are within the capabilities of anyone who does not have "two left hands," as the saying goes.

After each tube-bending operation, it is advisable to reheat an area larger than the bend itself and then allow the glass to cool slowly. This operation helps to eliminate internal stresses within the glass, stresses that weaken the bent area.

ADDENDUM 4

Building a Cooling Circuit or Water Aspirator That Uses Very Little Water

The use of a condenser or a water-jet aspirator (water aspirator) in an amateur laboratory generally consumes a great deal of water. Two simple modifications, however, make it possible to reduce this consumption considerably.

To supply cooling water to a condenser at very low cost, it is sufficient to use a well-insulated container (such as a camping cooler) filled with water cooled by large cold packs. A thin flexible tube filled with water is then coiled within this cold mass, after which a closed circuit is established in which the cooled water circulates through the condenser by means of a simple aquarium pump. It is as simple as that!

As for the water-jet aspirator, used to obtain a vacuum or a strong flow of air through a tube, enormous amounts of water can also be saved by operating in a closed circuit. The main trick consists of placing the water-jet aspirator upside down, that is to say with its head downward, and drawing water through its theoretical outlet while inserting into the circuit a water pump powerful enough to generate a strong flow. The water, drawn upward through the "foot" of the aspirator, will have exactly the same effect as a strong stream of water sent under pressure downward through its head.

ADDENDUM 5

Cooling Mixtures

The following are a few mixtures capable of producing distinctly subzero temperatures. Many others exist, but they are often less convenient to use or require substances that are less common or more expensive. The temperatures given here are purely indicative because they may vary according to the starting temperature or slight differences in the composition of the mixture. The ice should always be finely crushed and the solids reduced to fine crystals. Small, inexpensive electric machines capable of producing finely crushed ice from ordinary ice cubes are now widely available and can be very useful for preparing such cooling mixtures.

From 0° to –20°C
1 part ice + 2 parts $CaCl_2$ (–10 °C)
4 parts ice + 1 part KCl (–12 °C)
1 part ice + 1 part NH_4Cl (–15 °C)
1 part ice + 1 part aceton (–15 °C)
1 part ice + 1 part NaCl (–17 °C)

Below –20°C
3 parts ice + 1 part NaCl (–21 °C)
1 part ice + 1 part KCl (–30 °C)
1 part ice + 1/3 part $MgCl_2$ (–33 °C)
1 part ice + 1.5 parts $CaCl_2$ (–45 °C)
1 part $Ba(OH)_2$ + 1 part NH_4Cl, both solids rapidly mixed together (–20 to –30 °C)
WARNING: Never use anhydrous $CaCl_2$ because with ice, it hydrates exothermically.

ADDENDUM 6

Choice of Crucibles

An amateur chemist may be inclined to believe that everything can be heated in a porcelain crucible and therefore see no reason to buy any other type. Unfortunately, this is not the case.

Everyone knows—or should know—that fluorides and hydrofluoric acid must never be handled in glass apparatus, since they may attack the glass to a greater or lesser extent. It is less well known that silica apparatus, especially tubes and crucibles, must not be heated in the presence of alkalis, magnesium, magnesium salts, carbon, or carbonates. Porcelain crucibles should likewise not be heated with strongly basic substances such as lime or baryta, or with substances that attack porcelain, such as fluorides and borax.

Iron and copper crucibles are unsuitable for acidic substances and for certain salts.

Even platinum crucibles, so highly prized by chemists despite their prohibitive cost, are not the universal solution one might imagine. They are unsuitable for strong bases such as potassium hydroxide or sodium hydroxide. Worse still, they may react in the presence of chlorine, sulfur, boron, arsenic, silicon, phosphorus, cyanides, or any substance capable of releasing these elements or compounds. They should also not be used for reactions liable to produce mercury or lead. Platinum crucibles should even be protected from flames producing large amounts of carbon, since hot carbon makes platinum brittle.

The maximum temperature that a crucible can withstand must also be taken into account, because some highly exothermic reactions may cause the temperature to rise very rapidly to extremely high values.

Since strongly alkaline substances frequently have to be heated, crucibles made of pure nickel, which are commercially available in many sizes and capacities, may be recommended for this purpose. Refractory clay crucibles are also well suited, particularly when very high temperatures are required. It should be remembered, however, that ordinary pottery crucibles cannot withstand temperatures above

approximately 900 °C.

Bibliographic reference for this addendum:
Prof. L. D'Or, *Exercices de laboratoire relatifs au cours de chimie générale*, 3rd series, Liège, Rodestra, 1940–1941, pp. 81–82.

ADDENDUM 7

Volume 7 of Paul Schützenberger's *Traité de Chimie* (1894) and Clément Duval's *Manipulations de chimie* (1933) are particularly valuable because they provide preparation methods for a great many chemical substances.

CONCLUSION

We have now reached the end of this guide. It could have been even longer and included many other experiments; but it could just as well have been shorter. Finding the right balance in this field is difficult, and it is therefore impossible to satisfy everyone.

I simply hope that the preceding pages will prove useful to teachers and enthusiastic amateur experimenters.

Once again, I must emphasize one essential point: chemistry requires, if it is to be practiced without (too much) danger, extensive theoretical knowledge that is far from elementary, as well as practical skills that can only be acquired through time and hands-on experience. Wisdom therefore recommends beginning with simple experiments requiring only basic equipment and relatively harmless chemicals before gradually progressing to more complex ones.

The Internet, and YouTube in particular, are full of explanations provided by amateurs who sometimes have nothing but their good faith and their ignorance to justify the nonsense they say or demonstrate. Here, a young man explains how to prepare nitric acid without heating; there, another uses a plastic water bottle to contain liquid nitrogen; elsewhere, someone has improvised an essential-oil extractor from an old metal pipe fitted with a PVC tube as a condenser. And I will say nothing of the teenager who imagines that ammonia can be collected over water, or the handyman who has built a Bunsen burner from an old piece of pipe! These are all unreasonable or absurd practices that should never be imitated or regarded as

reliable sources of information.

In the end, I hope that I have inspired a few vocations while discouraging those whose ideas about a science that demands, above all else, rigor and method, were based on misconceptions.

This page intentionally left blanck

This page intentionally left blanck

Inside Back Cover

This book was written for those who still believe that chemistry is something to be seen and experienced — not merely read about.

It brings together experiments, techniques, observations, and practical ideas gathered over many years of work in the private laboratory of an enthusiastic amateur chemist.

Some of these are well known, others less familiar, and a few have almost disappeared from modern chemistry books.

They are presented here in the hope of awakening curiosity, encouraging experimentation, and sharing the fascination that chemistry has always held for the author.

Above all, this book is an invitation to explore seriously.

The author would be delighted if, through reading this book, some readers were inspired to pursue a career in chemistry.